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Chemical Composition of Exhaust Particles from Gas Turbine Engines

Pratt and Whitney Aircraft Group, East Hartford, CT

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16. ABSTRACT

A program was conducted to chemically characterize particulate emissions from a current technology, high population, gas turbine engine. Attention was focused on polynuclear aromatic compounds, phenols, nitrosamines and total organics. Polynuclear aromatic hydrocarbons (PAH) were determined by HPLC, GC/MS and NMR techniques. Phenols and nitrosamines were isolated and then measured by gas chromatographic methods utilizing flame ionization detection and nitrogen detection. Total organics were determined by a backflush chromatographic procedure. The particulate matter was collected using a high capacity pumping system incorporating 293 mm diameter Teflon filters through which was passed up to 43 m^3 of exhaust gas. Extraction of the organic matter was performed in a Soxhlet extractor using hexane. The engine was operated at idle, approach, climb and take-off power settings with low sulfur (0.007%S) and high sulfur (0.25%S) fuels. Most of the PAH were small 3-to-4 fused ring species. No nitrosamines were found and except in a few cases, at low levels, no phenols. PAH and total organic levels decreased with increasing power setting and were more concentrated in the exhaust from the low sulfur fuel. Less than 1% of the organic matter emitted from the engine was adsorbed on the particulate matter.

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CHEMICAL COMPOSITION OF EXHAUST PARTICLES FROM GAS TURBINE ENGINES

by

D. J. Robertson, J. H. Elwood, and
R. H. Groth

UNITED TECHNOLOGIES CORPORATION
Pratt & Whitney Aircraft Group
Commercial Products Division
East Hartford, Connecticut 06108

EPA Contract 68-02-2458

Project Officer

J. N. Braddock

Emissions Measurement and Characterization Division
Environmental Science Research Laboratory
Research Triangle Park, N.C. 27711

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PREFACE

In order to assess accurately the risks involved in the emission of particulate matter from aircraft gas turbine engines, the U. S. Environmental Protection Agency must, in addition to quantifying the mass emissions of particulate matter from such sources, determine the chemical composition of these particulates. It has been known for some time that fossil fuel-fired combustion sources emit a number of substances which exhibit varying degrees of toxicity; some of these substances such as certain polycyclic organic compounds and selected nitrosamines are thought to be carcinogenic. Although there have been no extensive studies performed to date, there is reason to believe that aircraft gas turbine engines burning conventional aviation fuels also produce these substances.

Limited testing to date, both at Pratt & Whitney Aircraft and through other agencies, however, indicates very strongly that concentrations of toxic substances in turbine particulates are extremely low. This necessarily imposes a requirement for trapping large amounts of sample in order to ensure that an adequate amount of material is available to perform a reliable qualitative analysis. The amount of total sample required must be determined from the sensitivity of the analytical methods used, as well as from the concentration, known or estimated, of the compounds of interest. In addition, the particulate collection apparatus design must take into consideration not only the collection of the material of interest but its preservation as well, both in character and quantity. Another consideration must also be the efficiency of the collection system and its ability to collect sufficient sample for chemical characterization within a reasonable amount of testing time. Any attempt to meaningfully characterize particulates from aircraft gas turbine engines must necessarily employ the use of high efficiency, high-flow rate, filtration techniques. It is clear that a simple filtration scheme employing the use of a device such as the EPA/SAE smoke meter will not be sufficient. While no such schemes have been shown to be completely satisfactory for sampling gas turbine engines, there are a number of promising approaches available.

Under this contract an appropriate high volume sampling system was designed which was used to collect particulate samples from the exhaust of a Pratt & Whitney Aircraft PT6A-45 Gas Generator. A series of comprehensive chemical analyses were performed to broaden our knowledge of the chemical nature of the organic material entrained on the particles.

ABSTRACT

Solid particulate matter, mainly carbon, emitted into the air from the combustion of fossil fuels contains a variety of organic species adsorbed on it. In order to assess the hazards associated with such emissions from small aircraft gas turbine engines burning conventional kerosene type fuels, a study was undertaken to collect and analyze exhaust particulates; in particular, polycyclic organic compounds and nitrosamines, some of which may be carcinogenic. As part of this effort, a high volume sampling collection system was developed to obtain an adequate amount of sample within a reasonable period of engine operating time due to the low concentrations of particulate and deletrious materials in the exhaust stream. The sampling system satisfactorily filtered up to 45 m^3 of exhaust gas. Although moisture and temperature problems interfered with the efficiency of the sampling system, it provided a qualitative analysis of the particulate. Collection of the particulates was made over a range of engine power settings at idle, approach, climb and takeoff, using low sulfur(0.00655% S)and high sulfur (0.25% S) fuels. Extraction of the organic matter from the sample was done in a Soxhlet extractor, usually using hexane, then analyzed by HPLC, GCMS, NMR and other procedures to determine the total organics adsorbed, the PAH content, and the presence of nitrosamines and phenols.

Total organics were determined by a backflush chromatographic procedure. This analysis showed that the organic material entrained on particulates emitted from gas turbines is a small fraction of the total organics emitted (less than 1%). Although this amount is a small fraction of the total organics emitted, it is significant because of the respirable nature of the particulates. Polynuclear aromatic hydrocarbons (PAH) were determined by GC/MS and high performance liquid chromatography (HPLC) techniques. Most of the PAH were non-carcinogens and were composed of the 3 to 4 fused ring compounds. The GC/MS technique identified specific compounds and the HPLC gave a good indication of the relative amounts of compounds in the 3 to 4 fused ring types versus the 5 to 6 fused ring types. The larger fused ring compounds existed in low concentrations. Phenols and nitrosamines were isolated and then measured by gas chromatography using a flame ionization detector and nitrogen detector. Nitrosamines were not found and the presence of phenols was detected at low concentrations. PNA and total organic levels decreased with increase in power setting and were higher in the exhaust from low sulfur fuels. Sulfur oxides measured by wet chemical techniques showed that a good material balance was obtained between fuel bound sulfur and the SO_2/SO_3 in the exhaust gases.

Results of this effort indicate that the sampling system shows good potential for the collection of particulates but that further development is needed for application of the system to larger gas turbine engines such as the JT8D. The program also identified the chemical analysis techniques and the type of future measurements which would yield meaningful data in the assessment of particulate emissions.

This report is submitted in fulfillment of EPA contract 68-02-2458 by United Technologies Corporation under the sponsorship of the Environmental Protection Agency. This report covers the period November 5, 1976 through March 31, 1978. The technical effort was completed in February 1978.

CONTENTS

Preface iii
Abstract iv
Abbreviations ix
Acknowledgment xi

Section 1. Introduction 1
Section 2. Conclusions 3
- Discussion of Conclusions 4

Section 3. Recommendations 6
- Discussion of Recommendations 6

Section 4. Technical Discussion 7
- Sampling System 7
  - Nature of the particulates to be sampled 7
  - Sampling methods 9
  - Design criteria 9
  - System hardware 9
  - Probe 11
  - System cooling 15
  - Filter materials 15
  - Sample degradation 16
  - Temperature control 18
  - Flow measurement 18
  - System operation 22
  - Packed bed filters 22
- Test Vehicle 23
  - Engine 23
  - Combustor 24
  - Test stand 24
  - Gas generator instrumentation 26
  - Emission instrumentation 27
- Trial Runs 29
  - Exit pipe mapping 29
- Test Procedure 35
  - Phase I 38
  - Phase II 39
- Sample Identification 40
- Mass Emissions Measurement Technology 42
  - Filters 43
  - Balance 43
  - Mass emissions testing 43
- Smoke Measurement Methodology 45
  - Conclusions 47
- Analytical Procedures 49
  - Sample treatment 49

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CONTENTS (Cont'd)

Organic analysis 50
Total organics 50
High performance liquid chromatographic analysis 55
Gas chromatograph-mass spectrometer analyses 68
Packed Bed Filter Studies 76
Nitrosamine analyses 89
Phenol analyses 91
Spectral data 94
    Nuclear magnetic resonance analyses 94
    Ultraviolet analyses 100
    Infrared analyses 106
Fuel analysis 107
Boiling point distribution 110
Sulfur oxides emissions 117
Proton activation analysis/x-ray analysis 139
Elemental analysis 142
References 144
Bibliography 147

Appendices

A. GC/MS Analysis of Polynuclear Mixes and Typical Turbine Combustor Exhaust 152
B. PNA Contribution from Filters and Solvents 158

ABBREVIATIONS

BAP	Benz (a) Pyrene
BP	Boiling Point
EI	Emission Index (lbs/1000 lbs fuel)
EPAP	EPA Emission Parameter (lbs/100 SHP/cycle)
ESFC	Effective Specific Fuel Consumption
ESHP	Equivalent Shaft Horse Power
F/A	Fuel to Air Ratio
GC/MS	Gas Chromatograph Coupled to Mass Spectrometer
HC/THC	Hydrocarbon Emissions
HP	Engine Horsepower
HPLC	High Performance Liquid Chromatograph
IR	Infrared
JT8D	P&WA Jet Turbine Engine
JT9D	P&WA Jet Turbine Engine
M	Molecular Weight
N_G	Gas Generator Speed
NMR	Nuclear Magnetic Resonance
NO_x	($NO + NO_2$) Emissions
P	Pressure
PAH	Polyaromatic Hydrocarbons
PNA	Polynuclear Aromatics
POM	Polynuclear Organic Material
PT6A-45	P&WAC Turbo-Prop Engine
SHP	Output Shaft Horsepower
SLS	Sea Level Static
T	Temperature
T_S	Gas Temperature at First Turbine Stage Exit
UV	Ultraviolet

w	Mass Flow
w_f	Gas Generator Fuel Flow
P	Pressure Drop
α	Atomic Hydrogen - Carbon Ratio of Fuel
δ	Ambient Pressure Ratio $\frac{P_o}{29.92}$
θ	Ambient Temperature Ratio $\frac{T_o}{59.0^{o}F}$

Subscripts

0	Ambient
1	Engine/Gas Generator Inlet
3	Compressor Inlet
4	Compressor Exit
5	First Turbine Stage Exit
7	Engine Exit
CB	Cabin Bleed

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SECTION 1

INTRODUCTION

The overall intent of this work was to aid the EPA and the industry in assessing the risk associated with the emission of particulates from gas turbine engines on which are adsorbed complex organic species. This work was accomplished during a 14 month program in three phases:

Phase I: Engine emission demonstration
Phase II: Exhaust particulate collection
Phase III: Chemical analysis and interpretation

The test vehicle selected for this program was the Pratt & Whitney Aircraft PT6A-45 gas generator which is representative of current production, high population small gas turbine engines.

An additional requirement of the contract called for the design and development of a high volume particulate collection scheme specifically adapted for gas turbine engine testing. This requirement is critical because experience has shown that the collection system used often defines the nature of the particulates collected. This can be especially true when working with volatile species such as polynuclear aromatic compounds (PNA).

The engine emissions demonstration phase provided data which demonstrated P&WA's ability to operate the test vehicle in a controlled and repeatable fashion with respect to power, gaseous emissions, smoke and particulate mass emissions. This was accomplished during a series of five trial runs over the usual power ranges (idle, approach, climb and takeoff).

More than 100 particulate samples were obtained for a wide variety of chemical analyses. These samples encompassed the whole range of engine power settings using the standard Jet A-1 fuel as well as Jet A-1 doped with 0.26% sulfur to evaluate the effects of fuel bound sulfur on emission characteristics. The effectiveness of the high volume sample system was limited only by the occasional high ambient dewpoint and temperature and by the need to control sample filter temperature in order to preserve the integrity of the volatile organic species.

A comprehensive chemical analysis of the organic material extracted from the particulate matter was undertaken with the primary emphasis on polynuclear aromatic hydrocarbons, especially those considered possibly carcinogenic. The analyses ranged from simple infrared and ultraviolet absorption spectroscopy to sophisticated nuclear magnetic resonance (NMR), computer aided combined gas chromatograph/mass spectrometer (GC/MS) and high performance liquid chromatography (HPLC). In addition, specific tests were performed to detect the presence of phenols and nitrosamines. The extremely low concentrations of significant organic species taxed the detection limits of many of the state-of-the-art analytical procedures.

Following the summary of major conclusions is a detailed description of the analyses performed and the results obtained.

SECTION 2

CONCLUSIONS

1. A high volume sampling system for collection of particulates from gas turbine engines was designed, fabricated and adapted to a Pratt & Whitney Aircraft PT6A-45 gas generator. The system collected a sufficiently large sample for the chemical analyses planned considering the low concentration (approx. 10 mg/m^3) of particulates in turbine exhaust.

2. Control of the sample collection system temperature and flow rate is essential due to the volatility of the organic species under investigation. Though this volatility is a known sampling problem, the high temperatures encountered in gas turbine sampling necessitate precise control and monitoring at the filter surface.

3. The purity of solvents and filters is critical at low levels and therefore purity must be established and maintained. Many spectroquality solvents and filters evaluated contained interfering substances which would severely bias the analytical results if used in sampling the small concentrations of organic species found in gas turbine exhaust.

4. Due to the extremely low concentrations of organic species found and the wide variations in sample humidity, temperature and flow conditions found in gas turbine exhaust, interpretation of the data should be primarily on a qualitative basis with little emphasis on the absolute numbers.

5. The organic material entrained on particulates emitted from gas turbine engines is only a small fraction of the total organics emitted. However, due to the respirable nature of the particulates, their analysis is of considerable significance.

6. The multitude of chemical analyses performed revealed the presence of numerous polynuclear aromatic compounds. Aromatic compounds with one ring or two fused rings were in an order of magnitude more abundant than the PAH having three or more fused rings. The vast majority of these compounds were the small, 3 to 4 fused ring compounds, with very few 5 to 6 fused ring compounds present. The concentrations were extremely low and very few of the compounds are known carcinogens. The maximum amount of polynuclear material in any one sample was less than 2 ppb. Total amount of carcinogens such as benz(a)pyrene and benzophenanthrene were an order of magnitude less.

7. No nitrosamines were found.

8. The presence of phenol was noted but at a very low concentration (part per trillion).

9. The concentrations of polynuclear aromatic hydrocarbons in the exhaust samples follow the overall hydrocarbon trend which decreases with increasing power setting.

10. Results obtained from very diverse analytical techniques, e.g., NMR, HPLC, GC/MS and total organic measurements were consistent.

11. A good material balance (within ± 6%) was obtained between fuel bound sulfur and the SO_2/SO_3 in the exhaust gases.

12. There was some indication that the levels of oxygenates and polynuclear aromatic hydrocarbons are higher in the low sulfur fuel exhaust samples.

13. The only known (2) carcinogenic PAH identified were benzofluoranthene, benzophenanthrene, and benz(a)pyrene. All of these compounds were below 0.1 parts per billion concentration.

DISCUSSION OF CONCLUSIONS

During the sampling operations in Canada, the ambient temperature and relative humidity varied considerably. As a result the temperature and moisture content of the exhaust also showed wide variations. Engine power setting also contributed to these variations. At lower power settings (idle) moisture condensed on the filters and seriously affected the flow characteristics of the filter. Consequently the amounts of particulate matter and adsorbed materials were lowered substantially. The total flows were thus only an approximation in some cases. The presence of variable amounts of moisture also affected the quantity of adsorbed matter. The results obtained were therefore a qualitative indication only and not an absolute quantitative assay.

The high volume sampling system was found to be satisfactory for filtering up to 45 m^3 of exhaust gas and to yield an adequate size sample in a reasonable time. Moisture and temperature problems with the sampling system represent areas of future development if quantitative data is needed. The system was adequate to provide a qualitative picture of the chemical nature of the particulate.

Measurement of the total organics and the PNA by gas chromatography-mass spectroscopy from packed bed filters (Chromosorb 102) showed that less than 1% of the organic material is adsorbed on the particulate matter and over 99% passed through the Mitex filter. This small amount however, could be carried along with the particulates and become lodged in the lungs. Thus, it could be of great significance from a health standpoint.

Polynuclear aromatic hydrocarbons were found by GC/MS and HPLC techniques. Mostly these PAH were non-carcinogens and of the 3 to 4 fused ring compounds. The GC/MS permitted specific identifications but the HPLC, under the conditions employed, did not fully resolve the complex mixtures. The HPLC did however give a good indication of the relative amounts of compounds in the 3 to 4 fused ring types versus the 5 to 6 fused ring types. Very few of the larger fused ring compounds were found and these were in very low concentrations.

Nitrosamines were not found but at the temperature occurring in the exhaust stream they would likely be unstable even if formed in the engine. Phenol analyses were limited to the several compounds for which the EPA procedure (EPA-650/2-75/056) was developed. This does not mean that other phenols or oxygenates are absent. The levels found and the occurrence in actual exhaust samples of these few phenols were low.The concentrations of PAH in the exhaust decreased with increasing engine power setting. This result was indicated by the data in the HPLC and GC/MS analyses. Because of sampling variations, this result should be considered qualitative. The general agreement between the two methods support the qualitative generalization. Similarly, a correlation between, a) oxygenate level and PAH level, and b) the sulfur levels in the fuels used is also supported by these two measurement techniques. Total organics measurements further corroborate the trend of higher organics with low sulfur fuel and with lower engine power setting.

Both gas flow and temperature elevation reduce the collecting efficiency for benz(a)pyrene. An even more serious loss would occur with lower molecular weight (fewer fused rings) compounds. Therefore, the temperature of collection is very critical.

Sulfur oxides measured in the exhaust gases by wet chemical procedures agree well with the sulfur analyses of both the high sulfur and low sulfur fuels. This suggests that virtually all of the sulfur is emitted as SO_2/SO_3.

SECTION 3

RECOMMENDATIONS

1. Advanced design work on the sampling system should be carried out to improve flow measuring characteristics, temperature regulation and collection efficiency to obtain more quantitative and reproducible data.

2. The present sampling system should be adapted to measure the mass emissions and chemical characteristics of particulates emitted from a high population, large gas turbine engine such as the JT8D and JT9D.

3. Future measurements should be extended to include materials collected on packed bed filters, such as Chromosorb 102 followed by cryogenic trapping to evaluate the efficiency of collection.

4. The analytical technique for organic materials measurement should be limited to gas chromatography, high performance liquid chromatography and gas chromatograph/mass spectrometry.

5. Analysis such as boiling point determination, NMR, UV, IR and elemental should be omitted since they yield information of limited value.

DISCUSSION OF RECOMMENDATIONS

The current sampling system was found to have problems associated with flow measurement, humidity and temperature control. For a sampling system to be adapted to large engines such as the JT8D, specific parameters must be considered, such as time available for sampling and temperatures associated with the exhaust stream.

The high population engine such as JT8D is more likely to be subject to regulation and for this reason, as well as for its greater usage, the nature of its effluent both adsorbed on the particulate matter and also that portion collected on the packed bed filter must be determined. Some early GC/MS analyses of samples from an JT8D style experimental combustor showed the presence of some of the same PNA compounds and should be investigated further. Some details of this work are given in Appendix A. Preliminary studies have shown that under 1% of the total sample, organics and PNA are adsorbed on the particulates. Additional material may pass through the packed bed filter and hence cryogenic trapping is suggested to recover it.

The analyses which yielded the most significant information in this study were, phenol-nitrosamine, HPLC, total organics and GC/MS. Other analysis specifically: boiling point determination , NMR, UV, IR, and elemental gave little useful information for these complex mixtures.

SECTION 4

TECHNICAL DISCUSSION

SAMPLING SYSTEMS

Nature of the Particulates to be Sampled

In spite of the considerable amount of work done by Pratt & Whitney Aircraft Group, Division of United Technologies Corporation and others(1), there is little agreement as to what is considered particulate matter. If particulate matter is collected simultaneously using existing techniques, there is little likelihood of agreement in terms of the absolute amounts and composition of the material collected. Therefore, it has become the practice to define particulates in terms of the method of collection and analysis. Considerable work is being done in government and private agencies to standardize a method of measurement and to interpret what the method actually does. However, this current program has contributed to and enhanced our understanding of particulate emissions.

Particulate matter emitted in the exhaust of gas turbine engines is known to consist of aerosols, finely divided carbon and other particles. Aerosols are typically made up of unburned and partially burned fuel, sulfates formed from the sulfur in the fuel, trace elements normally found in fuel, water droplets containing combustion byproducts, material ingested into the engine inlet, and materials attributable to normal wear processes in the engine. All of these particles may have possible toxicological or carcinogenic effects. For the various classes of organic species likely to be present, the anticipated variability in toxicity and perhaps smog forming capability makes it desirable to obtain specific qualitative and quantitative detail. Many of the particulates mentioned have polycyclic organic matter (POM) associated with them. These POM compounds are made up largely of complex organic hydrocarbons whose structure includes three or more fused rings, possibly aromatic. Some of these compounds have shown some evidence of carcinogenic effects when applied to rats, and there is some thought that similar effects might be obtained in humans(2).

Polycyclic organic matter is highly reactive, and considerable care must be taken in handling to preclude or minimize sample degradation. Sulfur trioxide, along with other atmospheric oxidants, and photo-oxidation will degrade these POM compounds. Degradation reactions are particularly accelerated when the compounds are adsorbed on carbonaceous material such as is found in gas turbine engine exhaust. The collection and preservation of POM compounds for analysis requires special attention, particularly to prevent the loss of volatile organic compounds(2).

A considerable body of evidence has been accumulated in recent years suggesting that POM compounds are found as normal by-products of fossil-fuel systems. It is anticipated that gas turbine engines are no exception. For example, studies at Moscow Airport resulted in the finding of benz(a)pyrene (BAP) which was attributed to jet aircraft. Similarly, earlier work performed under sponsorship of the Air Force School of Aerospace Medicine and at Pratt & Whitney Aircraft, resulted in the identification of a number of POM compounds in gas turbine combustor exhaust (3,4,5,6,7,8,9).

Evaluation of airborne particulate matter has resulted in the identification and classification of numerous compounds, of which several are suspected of being strongly to mildly carcinogenic. Investigation of these compounds has resulted in a number of analytical methods for their measurement and in an understanding of the requirements for sampling, sample handling, and the quantity of material required for analysis (10,11,12,13,14,15,16).

The many studies of diesel and automotive exhaust sources have resulted in the identification of a number of POM compounds, and it is logical to extend these investigations to gas turbine aircraft powerplants.

It is also known that the amounts and types of POM compounds present in automotive exhaust are dependent upon the fuel used and the fuel-to-air-ratio. Tests have shown that fuel that is rich in aromatics, produces more POM compounds, particularly polynuclear aromatic (PNA) compounds, than does fuel having less amounts of aromatic compounds. In addition, certain amounts of nitric oxide in the exhaust will lower the PNA content. It is reasonable to assume that the same phenomena will hold for gas turbine engines.

In addition to organic compounds such as POM, there are other substances of interest in the exhaust. The presence of nitrosamines (known carcinogens) has been reported in food, air, water, and diesel exhaust. It seems likely that they would also occur in the combustion by-products of gas turbine engines. As in POM compounds, it is anticipated that the nitrosamines will be present in very small quantities, necessitating large volume sampling. However, like POM compounds, although present in very small quantities, nitrosamines may still have environmental impact due to high toxicity or carcinogenicity. Analytical techniques have been developed recently which permit the separation and measurement of the various nitrosamine compounds (17,18,19,20,21).

Other materials found in aircraft gas turbine exhaust are more well known and do not pose any particular problems in either collecting or analyzing samples; however, problems can be encountered in obtaining samples for sample weighing. A significant portion of the sulfate fraction collected on a sample can be attributed to sulfuric acid, which is extremely hydroscopic. Extreme care, therefore, must be taken in handling and weighing of the filters (22,23).

Sampling Methods

Our experience has been that particulate materials in gas turbine engine exhaust are found in concentrations on the order of 5 to 10 milligrams per cubic meter. In collecting particulate samples for the separation and identification of organic compounds, using glass fiber filters, we have determined that a minimum of thirty-five cubic meters of exhaust gas should be filtered to allow for quantitative as well as qualitative analysis for organics obtained by Soxhlet extraction of the glass fiber filters (24).

Filtering this much exhaust gas using ordinary EPA filtering techniques requires a large amount of time, necessitating long engine operation times that would result in making sample collection prohibitively expensive. However, sampling time could be decreased by using a large filter (293 mm dia.) with a large capacity vacuum pump. A system capable of collecting enough sample material in less than 30 minutes of running time per sample point was considered a reasonable objective (25,26,27). Other factors were considered such as the possibility that volatile organic compounds, including some PNA and N-nitrosamines, would not be collected on the filter.

To investigate collection efficiency for the organic compounds, P&WA evaluated packed bed filters packed with polymeric beads. The polymeric beads were packed in a chromatographic type column capable of handling sufficient sample flow (28,29). The polymer columns were returned to the P&WA Physics and Chemistry laboratory and the organics were extracted using the standard Soxhlet apparatus.

Design Criteria

The High Volume Sampling System was designed on the assumption that 5-10 mg/m^3 exhaust particulates would be found at the exhaust plane of the PT6A-45. It was also assumed that to accomplish sampling in a reasonable time period (approximately 1/2 hour) and to achieve the estimated 0.5 grams sample considered desirable for organic analysis, a sampling rate of about 3.3 m^3/min would be necessary.

It was initially considered necessary to reduce the sample gas temperature from a 1580^{o}F maximum at takeoff to no more than 250^{o}F at the filter surface. Sample degradation studies conducted after the sampling system was constructed, indicated that the filter temperature should be further reduced to 160^{o}F. To reduce the sample temperature, a significant degree of water cooling was considered necessary. However, at the same time sample residence was kept below 5 seconds in the sample lines to minimize sample loss on the walls of the sampling system.

System Hardware

A sampling system shown schematically in Figure 1 was designed in which the pressure at the exhaust plane provided a portion of the sample flow. This flow was augmented by use of a Roots* 3514J vacuum blower (Figure 2).

*Dresser Industries, Connersville, Ind.

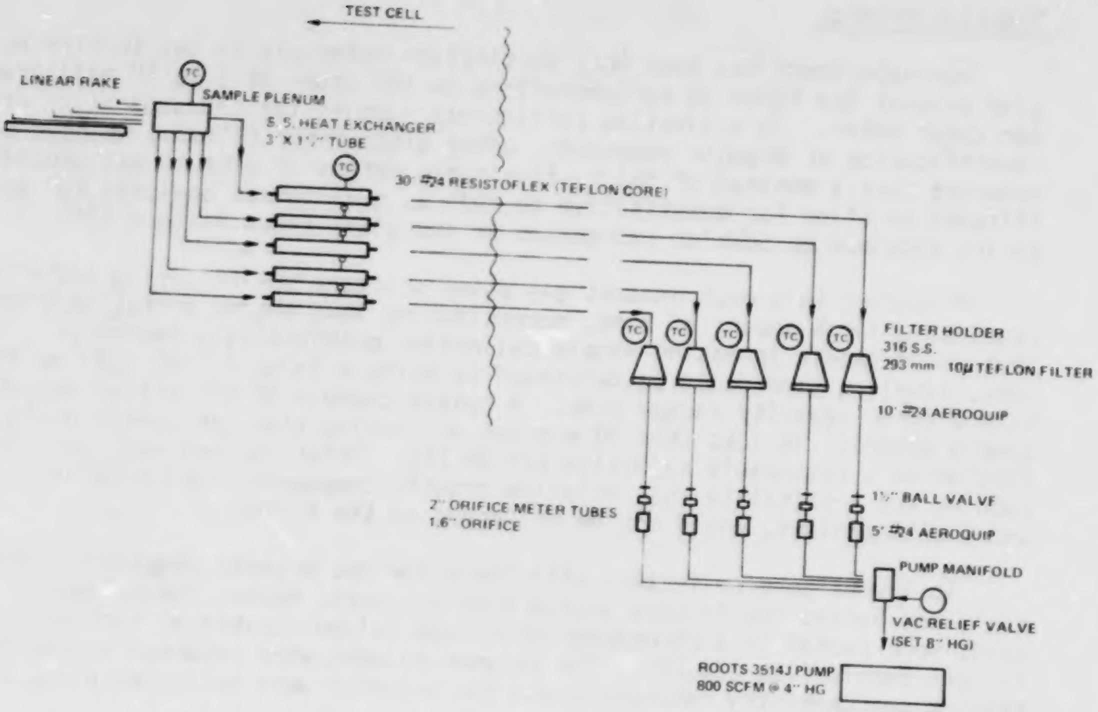

TEST CELL
LINEAR RAKE
TC
SAMPLE PLENUM
S. S. HEAT EXCHANGER
3' X 1½" TUBE
30' #24 RESISTOFLEX (TEFLON CORE)
FILTER HOLDER
316 S.S.
293 mm 10μ TEFLON FILTER
10' #24 AEROQUIP
1½" BALL VALVE
2" ORIFICE METER TUBES
1.6" ORIFICE
5' #24 AEROQUIP
PUMP MANIFOLD
VAC RELIEF VALVE
(SET 8" HG)
ROOTS 3514J PUMP
800 SCFM @ 4" HG

Figure 1. High volume sampling system block diagram.

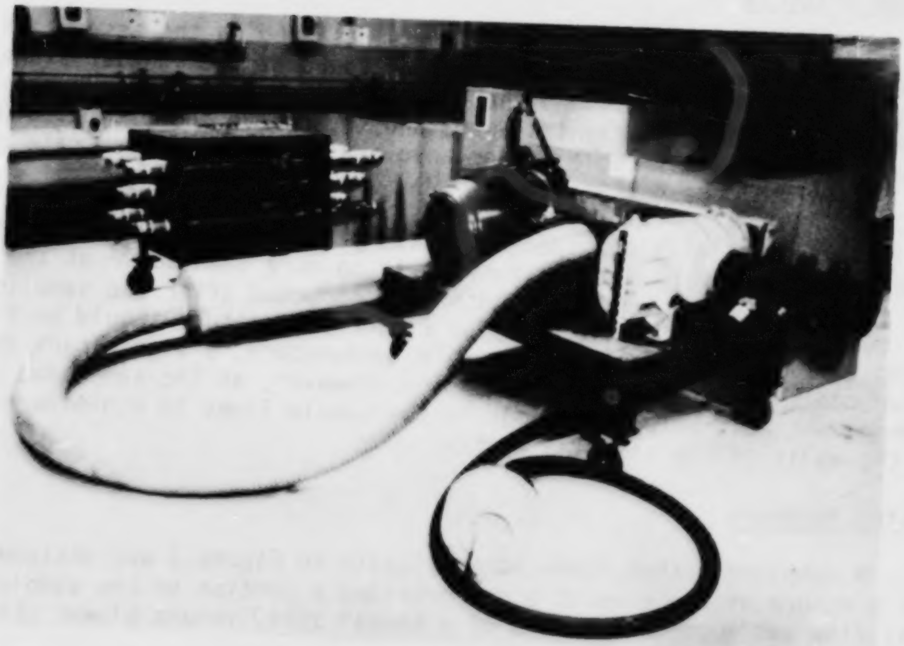


Figure 2. Prototype high volume sample system components.

The blower was capable of 800 ft^3/min @ 4" Hg vacuum and was considered the primary driving force at idle, where ram pressure in the exhaust plane was minimal. Flow was monitored by a system of 5 orifice meter tubes with 1.6" orifices coupled to the exits of 5 cone shaped filter holders (Figures 3, 4, 5, 6) sized to accept 293 mm diameter circular filters. Sample lines were 1" 316 stainless steel to the final heat exchanger. After this point lines were 1-1/2" Resistoflex (Teflon core).

Probe

The probe designed was a five point linear rake (Figure 7, 8) mounted in an 18-inch section of exhaust duct (Figure 9, 10) immediately behind the engine. The probe elements were 3/4-inch I.D. 316 stainless steel tube set at centroids of equal area within the duct and reinforced at critical stress points with Hastalloy. It was calculated that 3/4-inch orifices would be necessary to avoid a choked flow condition at idle at 3.3 m^3/min per filter element. The 316 stainless steel proved to have sufficient temperature tolerance to avoid high temperature oxidation throughout the test program.

The five tubes of the linear rake were coupled to a 12-inch mixing plenum outside the exhaust duct. This plenum was designed to average out any differences in sample composition between each of the five probe elements. Some radiational cooling of the exhaust gas was also expected.

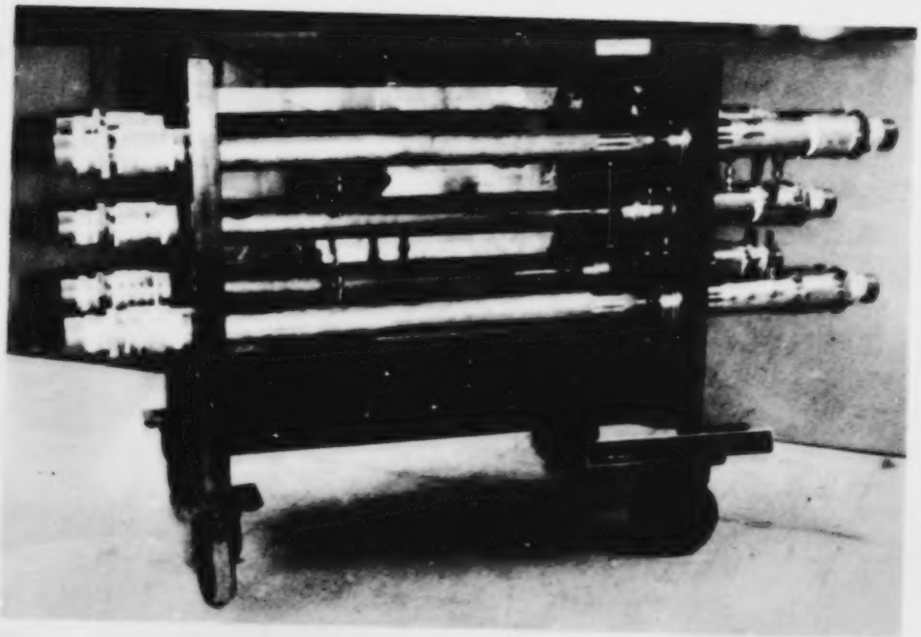


Figure 3. Orifice meter flow measuring tubes.

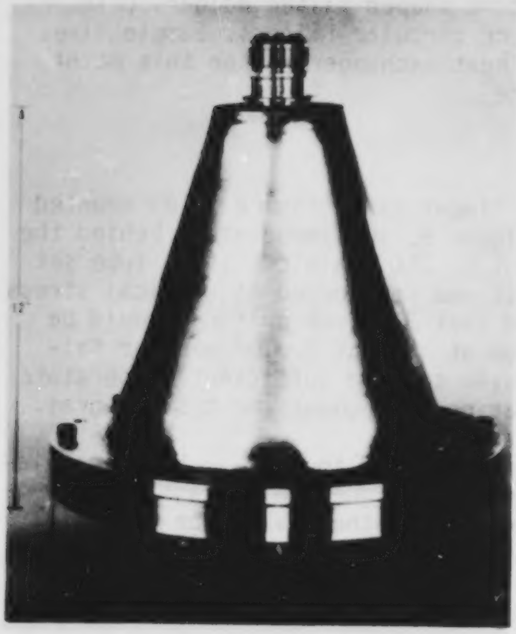


Figure 4. 293 mm filter holder assembled.

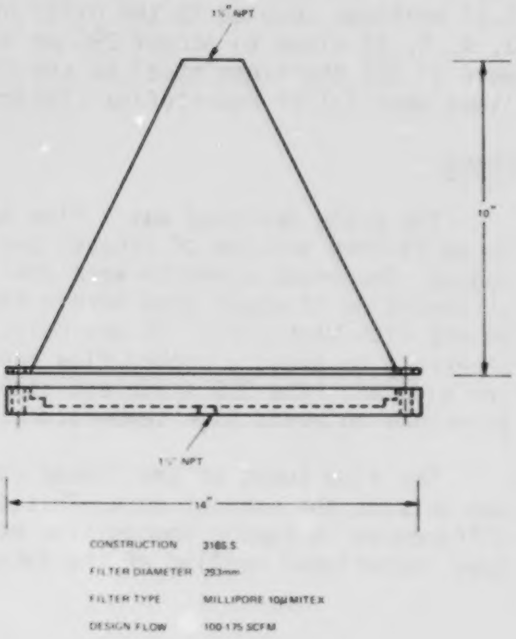

1½" NPT
10"
1½" NPT
14"
CONSTRUCTION 316S S
FILTER DIAMETER 293mm
FILTER TYPE MILLIPORE 10μ MITEX
DESIGN FLOW 100-175 SCFM

Figure 5. High volume filter holder assembly.

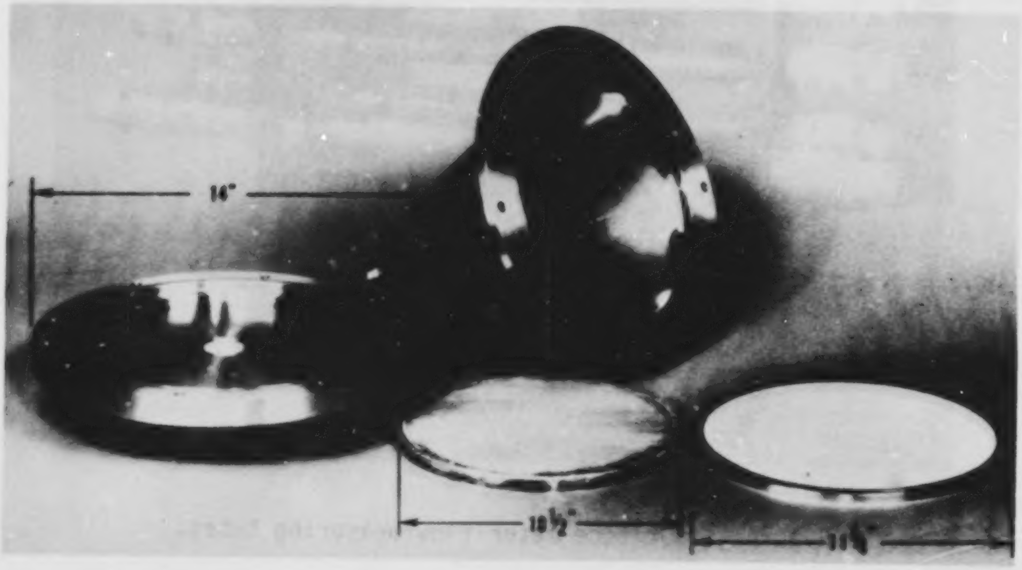


Figure 6. 293 mm filter holder disassembled.

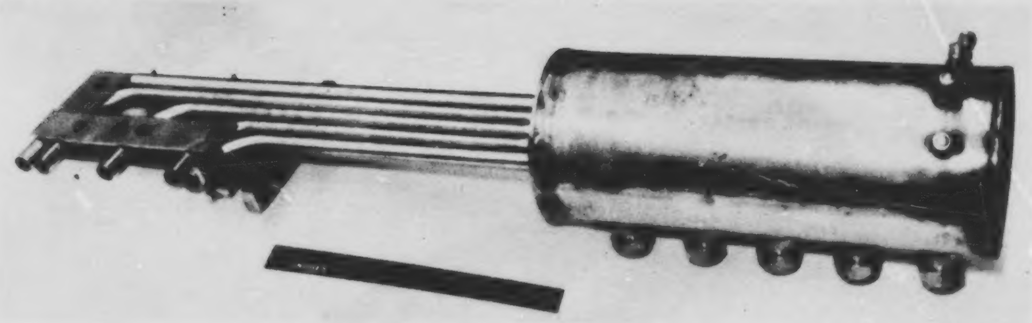


Figure 7. Sample rake and plenum chamber.

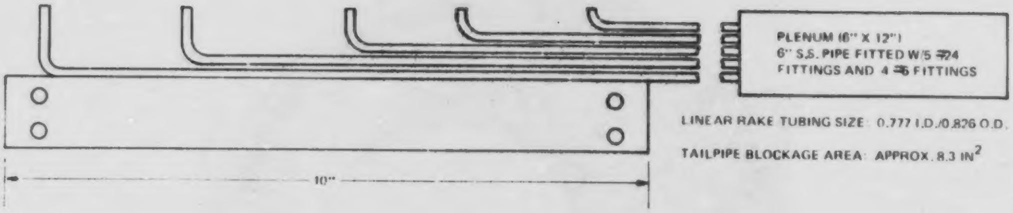

PLENUM (6" X 12")
6" S.S. PIPE FITTED W/5 #4
FITTINGS AND 4 #6 FITTINGS
LINEAR RAKE TUBING SIZE: 0.777 I.D./0.826 O.D.
TAILPIPE BLOCKAGE AREA: APPROX. 8.3 IN²
10"

Figure 8. Linear rake and sample plenum.

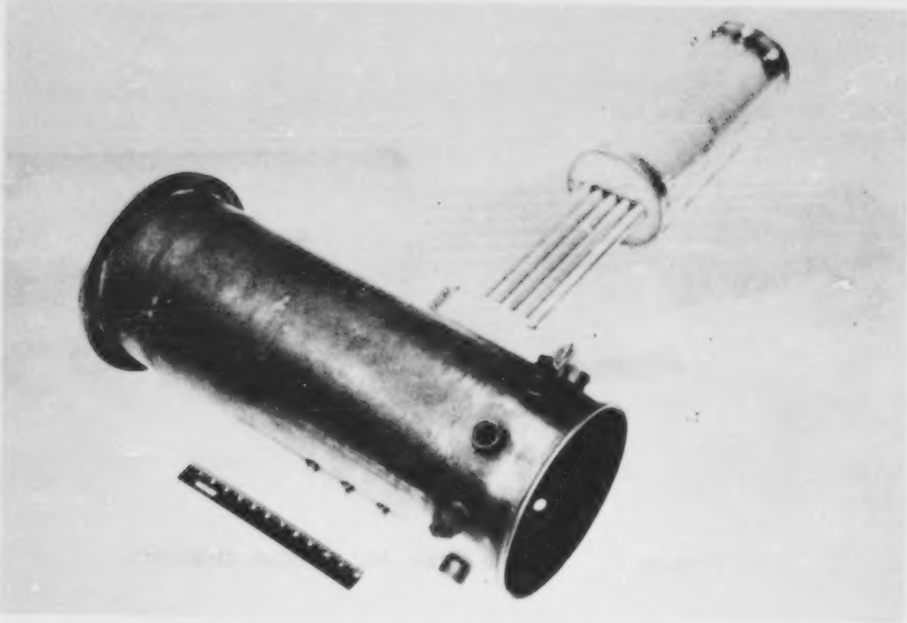


Figure 9. Rake installed in exhaust duct.

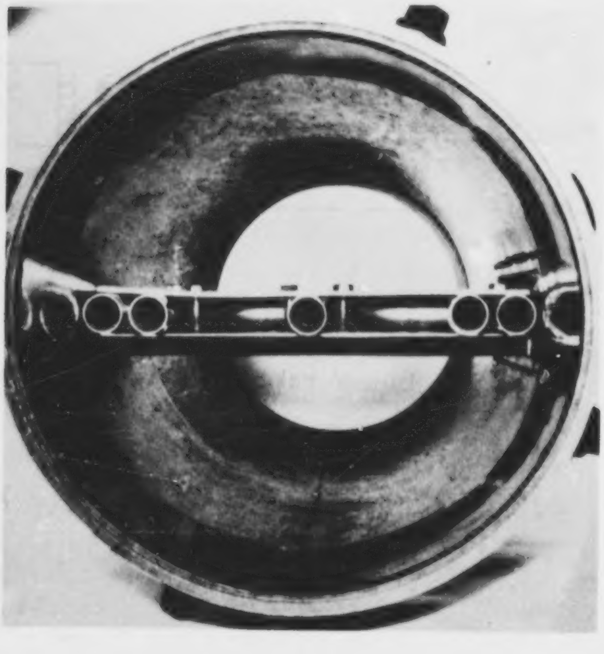


Figure 10. Sample probe in exhaust duct.

System Cooling

It was initially planned to cool the sample gas using a 4 foot long water cooled heat exchanger (Figure 11). During the testing, this proved to be insufficient for cooling. Additionally, the degree of radiational cooling anticipated to occur before the heat exchanger was below expectations. Prior to the test program, the heat exchanger was enlarged by adding approximately 20 feet additional stainless steel tubing placed in a water filled trough. The water flow in this trough and consequently the temperature was continuously variable and controllable. The entire distance from the sample plenum at the probes to just ahead of the filter housings was water cooled and this cooling was found to be sufficient at all power settings.

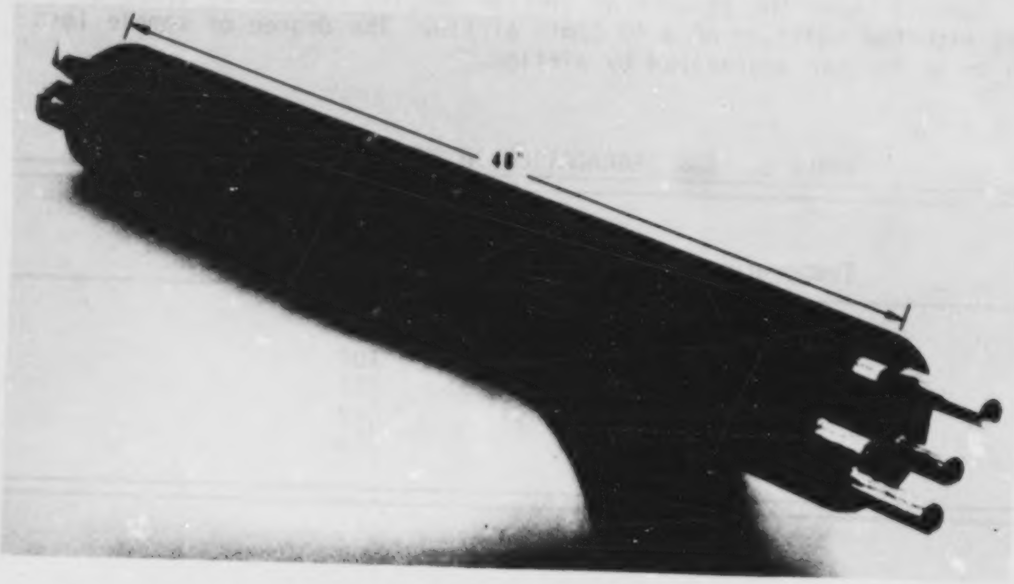


Figure 11. Heat exchanger.

Filter Materials

A number of filter materials were examined for stability at temperatures up to 250°F, solvent compatibility and interfering substances when subjected to HPLC analysis for PNA. Filters considered were standard Millipore, PVC, Mitex, Fluoropore, Gelman type A glass fiber, type E, type A-E, and Nuclepore. Mitex, a pure Teflon filter, was ultimately chosen for its total absence of interfering contaminants, its high temperature and solvent compatibility and its high strength. Use of a Gelman type A-E filter, fired at 500°C for 1 hour to combust contaminants, was considered. It was free of contaminants and was compatible with high temperature, however, its mechanical strength was so reduced as to make use of these filters undesirable.

Details of a preliminary study on solvent and filter selection for PNA analysis are given in Appendix B.

Sample Degradation

To best determine the maximum desirable filter temperature during test, a series of experiments was conducted to measure percent sample recovery of BAP after exposure to elevated temperature and airflow. Table 1 shows the results of placing 0.0050 mg BAP in a pyrex disk in an oven for 30 minutes at temperatures ranging from 72°F to 230°F. Sample loss is apparent above 160°F. Table 2 shows the results of placing 47 mm Mitex filters doped with 0.0050 mg BAP in an oven for 30 minutes at temperatures ranging from 72°F to 230°F. Considerable loss is seen to occur at some point between 130°F and 160°F. This is a "worst case" situation since the presence of carbon (typical of turbine exhaust) would reduce the losses substantially. Table 3 shows the results of similar samples exposed to temperature, but with the addition of a 40 l/min airflow. The degree of sample loss is shown to be further aggravated by airflow.

TABLE 1. BAP DEGRADATION IN PYREX DISHES

Temperature	Percent Recovery
72°F	100
130	102
160	77
200	72
230	18

TABLE 2. BAP DEGRADATION ON MITEX FILTERS

Temperature	Percent Recovery
Baseline Blank	100
72°F	94
130	97
160	66
200	62
230	38

TABLE 3. BAP DEGRADATION ON MITEX WITH AIRFLOW*

Temperature	Percent
Baseline Blank	100
72°F	93
175	36
218	22

*40 liters/min

Figure 12 graphically illustrates the effect of temperature on sample recovery under the conditions described above. BAP on Mitex and with airflow suffers the greatest sample loss at any given temperature when compared to the effects of temperature on BAP alone and BAP on Mitex.

Based on the above findings, it is theorized that lower molecular weight substances may volatilize more readily than BAP and at a lower temperature, thus contributing to sample loss at temperatures well below the 160°F taken as a maximum sampling limit.

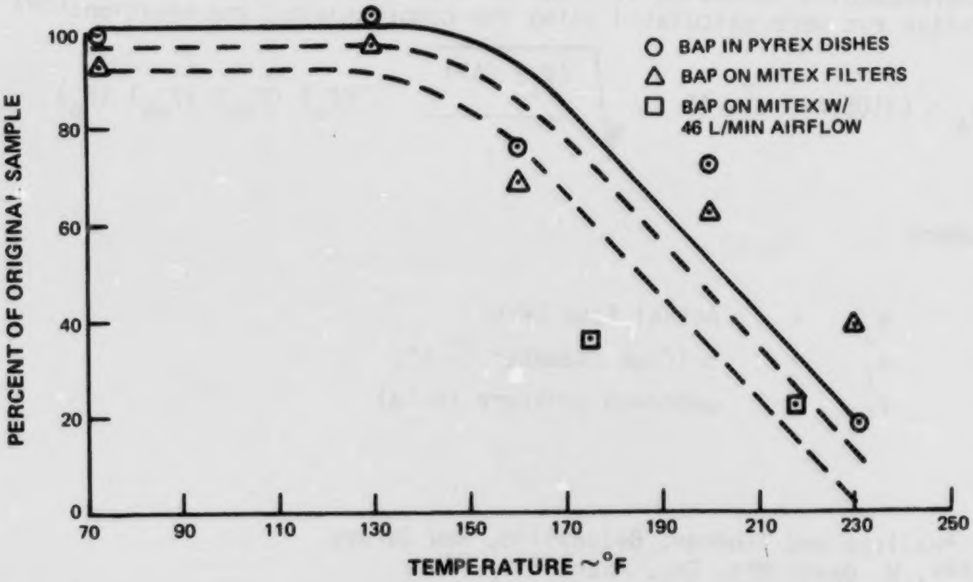


Figure 12. Effect of temperature on sample recovery.

Temperature Control

Temperature control involved the controlled metering of cooling water through the cooling trough and heat exchanger while instantaneous control was achieved by varying the sample flow to each filter using 1-1/2-inch ball valves. A chromel-alumel thermocouple located 1/2-inch above the center of each filter was used for temperature measurement. At no time was the temperature permitted to exceed 160°F. This maximum was considered a critical factor and was based on a balance between data obtained in the BAP degradation studies and a need for obtaining a sizeable quantity of particulate matter.

The temperature control maximum of 160°F hindered test point starts especially at idle and approach. At start-up the filter housing temperature was below the dew point of the sample gas, enough to condense water and wet the filters. Under these circumstances, flows often could not be increased sufficiently to bring the housing and filter above the dew point of the sample gas. An alternative start-up approach which reduced but did not eliminate the problem was to empty the trough and heat exchanger and start the flow of cooling water only after the gas temperature had brought the filter housings to 160°F. In this way most of the wetting could be avoided and flows could be maintained at diminished yet respectable levels.

Flow Measurement

Flows were measured using a system of five orifice meter tubes coupled to the exit of each of the five filter housings. Absolute pressure was measured upstream of the orifice plate using a Wallace and Tiernan* gauge. ΔP across the orifice was measured using a system of Magnehelic** gauges and upstream and downstream temperatures were measured using chromel-alumel thermocouples connected to a Doric⁺ digital readout. Flow data for each filter run were calculated using the compressible flow equation:(30)

$$W_a = (3105.44)\ d_1^2\ AE \sqrt{\frac{(P_1)\ (\Delta P)}{T_1}}\ (F_a)\ (F_{pv})\ (F_{wv})\ (F_p)$$

where

W_a = Actual flow (#/hr)
d_1 = orifice diameter (1.6")
P_1 = upstream pressure (psia)

---

*Wallace and Tiernan, Belleville, New Jersey
**F. W. Dwyer Mfg. Co., Mich. City, Ind.
+Doric Scientific, San Diego, Calif.

ΔP = pressure drop (psi)

T_1 = upstream temperature (^{o}R)

F_a = area factor correction

F_{pv} = Supercompressibility correction

F_{wv} = water vapor correction

F_p = density correction

E = Expansion factor

A = Coefficient of discharge

Water was a problem in the recording of flow data. Orifice meter tubes at idle and at approach often operated below the dew point of the gas and as a consequence, the pressure taps to the Magnehelic gauges (ΔP) filled with water and failed to operate properly. The tubes were emptied of water whenever the problem ocurred; however, some uncertainity as to the actual flow does exist for some test points at low power. The data in every case was examined for discrepancies in ΔP between filters in the same test run and corrected to the test point average where a Magnehelic gauge was clearly inoperative.

Figure 13 illustrates the typical flow variations experienced from the start of a test run. Effects encountered in the first ten minutes of every test run were those of temperature and the flow reduction required to stay within the 160°F maximum. Particulate loading also reduced flow with time.

Table 4 gives sampling time, tailpipe temperature, plenum temperature, filter surface temperature and total flow for each filter sampled. Sampling times ranged from 30 to 95 minutes, filter surface temperatures ranged from 89°F to 161°F and total flow ranged from 12.9 m^3 to 50.8 m^3.

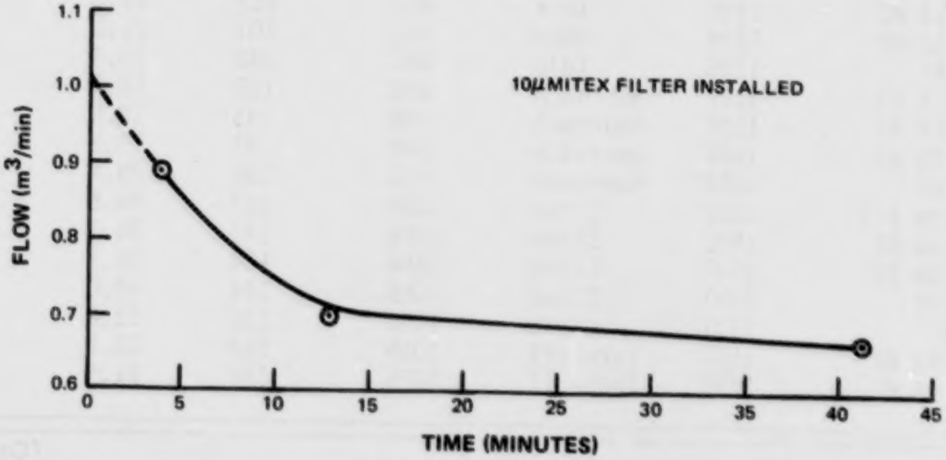


Figure 13. Typical flow variations while running.

TABLE 4. SAMPLING CONDITIONS

Filter Identification	Tailpipe Temp^{o}F	Power Setting	Plenum Temp^{o}F	Filter Temp^{o}F	Flow (m^3)	Sampling Time (Minutes)
LC/UV 1A #1	1208	Idle	643	127	26.4	60
P/N 1A	1208	Idle	643	130	26.1	60
IR 1A	1208	Idle	643	109	26.4	60
NMR 1A	1208	Idle	643	114	26.3	60
GC/MS 1A #1	1208	Idle	643	119	26.5	60
BP 1A	1219	Idle	702	114	24.6	65
T-ORG 1A #1	1219	Idle	702	116	24.5	65
EPA 1A	1219	Idle	702	109	24.6	65
EL 1A	1219	Idle	702	143	49.6	65
LC/UV 2A #1	1182	Approach	592	99	17.5	50
GC/MS 2A #1	1182	Approach	592	106	17.5	50
BP 2A	1174	Approach	658	105	22.7	63
T-ORG 2A #1	1174	Approach	658	109	22.7	63
EPA 2A	1174	Approach	658	103	22.7	63
EL 2A #1	1174	Approach	658	104	31.5	63
LC/UV 3A #1	1580	Climb	1086	129	32.4	45
GC/MS 3A #1	1580	Climb	1086	126	32.4	45
BP 3A	1580	Climb	1086	120	32.4	45
T-ORG 3A #1	1580	Climb	1086	114	32.4	45
EL 3A #1	1580	Climb	1086	137	42.3	45
P/N 3A	1578	Climb	1072	134	27.6	50
IR 3A	1578	Climb	1072	124	27.8	50
NMR 3A	1578	Climb	1072	109	27.8	50
LC/UV 4A #1	1578	Take-off	1050	142	32.2	37
GC/MS 4A#1	1578	Take-off	1050	149	32.0	37
BP 4A	1578	Take-off	1050	135	28.1	37
T-ORG 4A #1	1578	Take-off	1050	117	28.1	37
EL 4A #1	1578	Take-off	1050	139	32.2	37
LC/UV 1A #2	1235	Idle	697	109	21.0	55
GC/MS 1A #2	1235	Idle	697	112	21.0	55
T-ORG 1A #2	1235	Idle	697	107	21.0	55
EL 1A #2	1235	Idle	697	148	20.4	55
LC/UV 2A #2	1187	Approach	698	132	13.2	30
GC/MS 2A #2	1187	Approach	698	145	12.9	30
T-ORG 2A #2	1187	Approach	698	97	13.2	30
EL 2A #2	1187	Approach	698	166	29.4	30
LC/UV 3A # 2	1531	Climb	1056	127	36.5	42
GC/MS 3A #2	1531	Climb	1056	141	36.1	42
T-ORG 3A #2	1531	Climb	1056	108	26.1	42
EL 3A #2	1531	Climb	1056	114	42.0	42
EPA 3A	1531	Climb	1056	110	23.8	42
LC/UV 4A #2	1566	Take-off	1059	118	23.5	46
GC/MS 4A #2	1557	Take-off	1076	132	21.9	36

(Continued)

TABLE 4 (Continued)

Filter Identification	Tailpipe Temp°F	Power Setting	Plenum Temp°F	Filter Temp°F	Flow (m^3)	Sampling Time (Minutes)
T-ORG 4A #2	1566	Takeoff	1059	116	23.5	46
EL 4A #2	1566	Takeoff	1059	125	43.7	46
EPA 4A #2	1566	Takeoff	1059	115	23.5	46
GC/MS 4A #3	1557	Takeoff	1072	138	21.9	36
T-ORG 4A #3	1557	Takeoff	1072	124	18.1	36
EL 4A #3	1557	Takeoff	1072	144	43.0	36
LC/UV 4A #3	1557	Takeoff	1072	149	21.9	36
LC/UV 1B	1204	Idle	–	153	29.3	95
IR 1B	1204	Idle	–	112	29.4	95
NMR 1B	1204	Idle	–	145	29.3	95
GC/MS 1B #1	1204	Idle	–	118	29.3	95
BP 1B	1204	Idle	–	98	29.7	95
LC/UV 2B	1148	Approach	–	161	47.5	89
GC/MS 2B #1	1148	Approach		135	47.6	89
BP 2B	1148	Approach	–	126	47.9	89
LC/UV 3B	1531	Climb	–	141	42.4	60
GC/MS 3B #1	1521	Climb	–	161	50.8	65
BP 3B	1521	Climb	–	160	45.5	65
T-ORG 3B	1521	Climb	–	123	45.9	65
EPA 3B	1521	Climb	–	160	45.9	65
LC/UV 4B	1564	Takeoff	1042	131	92.7	54
GC/MS 4B #1	1564	Takeoff	1042	132	37.8	54
BP 4B	1564	Takeoff	1042	113	23.8	54
T-ORG 4B	1564	Takeoff	1042	94	27.5	54
EPA 4B	1564	Takeoff	1042	105	19.4	54
GC/MS 1B #2	1189	Idle	–	99	25.6	80
T-ORG 1B	1189	Idle	–	93	25.6	80
EPA 1B	1189	Idle	–	93	25.6	80
EL 1B	1189	Idle	–	154		80
GC/MS 2B #2	1148	Approach	–	148	47.5	88
T-ORG 2B	1148	Approach	–	119	47.5	88
EPA 2B	1148	Approach	–	134	47.5	88
EL 2B	1148	Approach	–	151	47.5	88
GC/MS 3B #2	1531	Climb	–	155	44.8	60
EL 3B	1531	Climb	–	155	42.2	60
NMR 3B	1531	Climb	–	136	39.7	60
IR 3B	1531	Climb	–	125	42.4	60
GC/MS 4B #2	1580	Takeoff	–	139	47.6	55
EL 4B	1580	Takeoff		138	47.2	55

System Operation

The high volume sampling system was found to operate in a manner consistent with its design objectives. Sufficient material was obtained to perform all but the elemental analysis. In this particular case, a different approach to the sample collection would have been necessary to obtain sufficient material for meaningful results by the analytical method used.

Sample temperatures were kept within the temperature maximum of 160°F found to be critical to BAP loss. The sampling temperatures experienced are believed to be the best compromise between temperatures so low as to render the system inoperable and temperatures high enough to volatilize the large majority of organic material entrained in the particulate matter.

The orifice meter tube approach to sample flow measurement was demonstrated to be essentially sound. However, an alternative scheme for measurement of ΔP would be desirable to eliminate uncertainties in this measurement.

Glass fiber filters would have provided considerable advantage in reducing the ΔP across the filter. This high ΔP compounded problems with start-up saturation of the filter with water and limited our use of the Roots vacuum blower (8" Hg limit) in augmenting flow at lower power settings. The low mechanical strength of fired glass fiber filters is, however, a considerable drawback to their use.

Packed Bed Filters

In addition to collecting particulates using the filter sampling system designed for this test, a packed bed sampling device (Figure 14) was used to sample relatively low exhaust gas volumes for both particulates and organic vapors. These optional measurements were made because certain amounts of organic material would be lost during any collection process designed for particulates only.

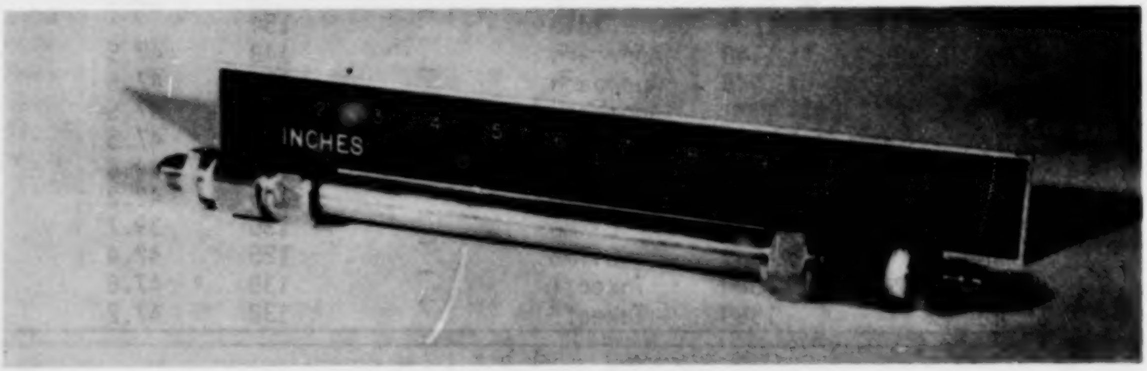


Figure 14. Packed bed sampling device.

The sampling device, a 1/2" O.D. x 6" long stainless steel tube was packed with 7 to 12 grams of Chromosorb 102. The sampling rate was approximately 0.035 cubic meters per minute. The samples were obtained directly from the sample plenum chamber shown in Figures 7 and 8.

TEST VEHICLE

The experimental version of a P&WA PT6A-45 gas generator was selected for the program since it is representative of current production, high population engines which are anticipated to be in production well into the 1980's. Over 10,000 engines of this type have been delivered to date. The following discussion describes the gas generator used in this program.

Engine

The PT6A-45 represents the largest and most advanced version of the PT6 engine series. Table 5 shows the ratings and performance parameters of the PT6A-45 engine.

TABLE 5. PT6A-45 PERFORMANCE PARAMETERS

Takeoff Rating	
SLS-Std. Day ESHP/SHP	1174/1120
Consumption ESFC	0.560
Propeller Speed RPM	
Takeoff	1620/1700 (max torque limited/max speed)
Cruise	1425
Mass Flow at T.O. lbs/sec air	8.6
Compressor Pressure Ratio	9:1

The compressor of the PT6A-45 consists of three axial stages combined with a single centrifugal stage. The combustion chamber is of the annular reverse flow type, with 14 fuel nozzles spraying tangentially. The first stage turbine downstream of the combustor drives the compressor. Combustor conditions are simulated with a back pressure valve downstream of the compressor turbine.

Combustor

The combustors in use with PT6A-45 engines are small and hence highly loaded (5.1 x 10^6 BTU/hr. atm. ft^3). They utilize 14 simplex fuel nozzles of Flow Number 1.9. Other characteristics of the combustor are shown in Table 6.

TABLE 6. PT6A-45 COMBUSTOR PARAMETERS (S.L.S.T.O.*)

Combustor mass flow (W_3)	8.6 lbs/sec.
Pressure (P_3)	9.0 atm.
Inlet Temperature (T_3)	1071°R
Outlet Temperature (T_4)	2460°R
Pressure Loss	2.3%
M_{ref}	0.0269
Outside Diameter (D_o)	15.71 in.
Inside Diameter (D_i)	11.65 in.
Length	5.41 in.
Combustor Volume	0.27 cft.
Temperature Pattern Factor	0.15 - 0.18

*Sea Level Static Takeoff Condition

A low emission combustor was used during the test program. Although the combustor profile is identical to the Bill-of-Materials configuration, the flow splits as well as cooling arrangements were modified to reduce exhaust emissions as well as improve combustor life. Figure 15 is an emissions profile of the low emission combustor.

Test Stand

The gas generator was tested in a facility shown schematically in Figure 16. The intake fan supplies are to the gas generator at pressures up to 1" of water. The intake air supply ensures uniform intake temperature distribution (5°F max variation) to the gas generator.

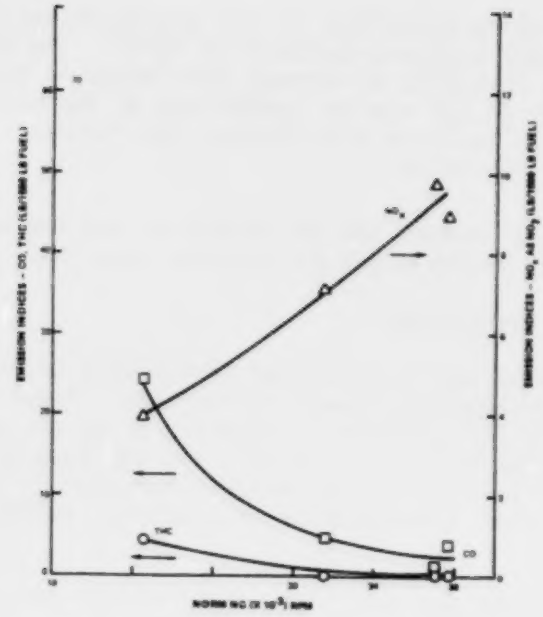


Figure 15. Emissions profiles from low emission combustor.

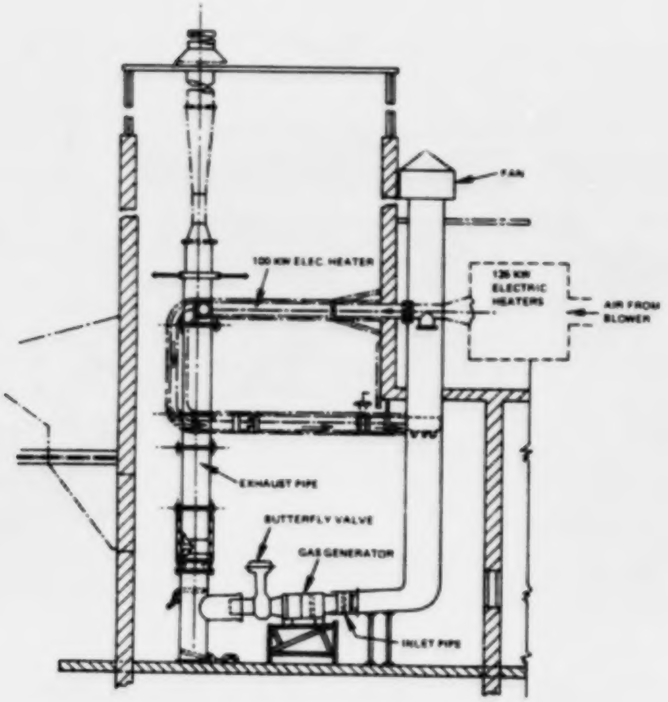

FAN
100 KW ELEC. HEATER
125 KW ELECTRIC HEATERS
AIR FROM BLOWER
EXHAUST PIPE
BUTTERFLY VALVE
GAS GENERATOR
INLET PIPE

Figure 16. Schematic of typical gas generator test facility.

Combustor operating conditions on the gas generator are set up with a remotely actuated back pressure (butterfly) valve. The exhaust from the gas generator tail pipe is led to an exhaust duct which is kept at reasonable temperatures through an air ejector downstream of the butterfly valve. The test facility is also equipped with heaters for increasing inlet air temperature during winter operation.

The exhaust pipe between the gas generator and the butterfly pipe was instrumented for gas analysis and particulate sampling.

Gas Generator Instrumentation

The gas generator was instrumented extensively to monitor all parameters normally required to evaluate performance. These included air and fuel flow rates into the combustor, temperatures at gas generator intake, combustor intake, compressor turbine exit and gas generator exit. The gas generator was also instrumented to measure combustor inlet (P_3) and outlet (P_4) pressures, so that determination of combustor pressure drops ($\Delta P/P$) can be made.

Photographs of the gas generator test facility and control panel are shown in Figures 17 and 18.

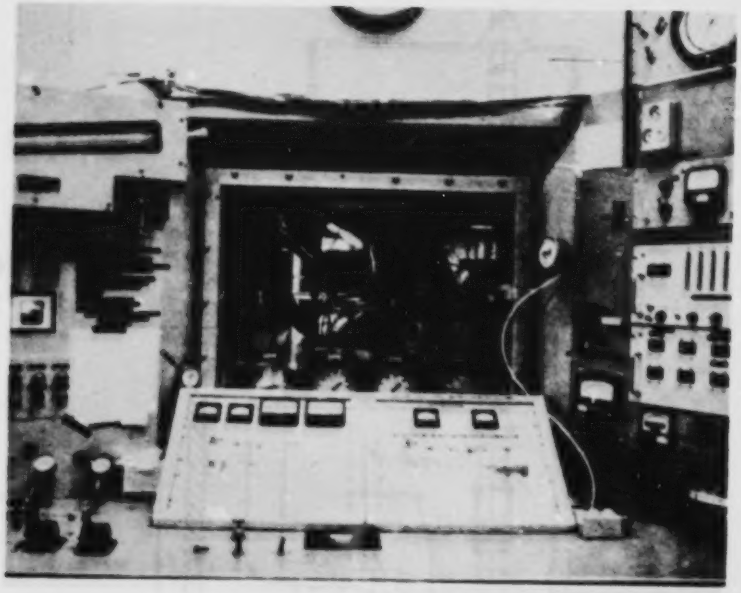


Figure 17. Combustor rig control room.

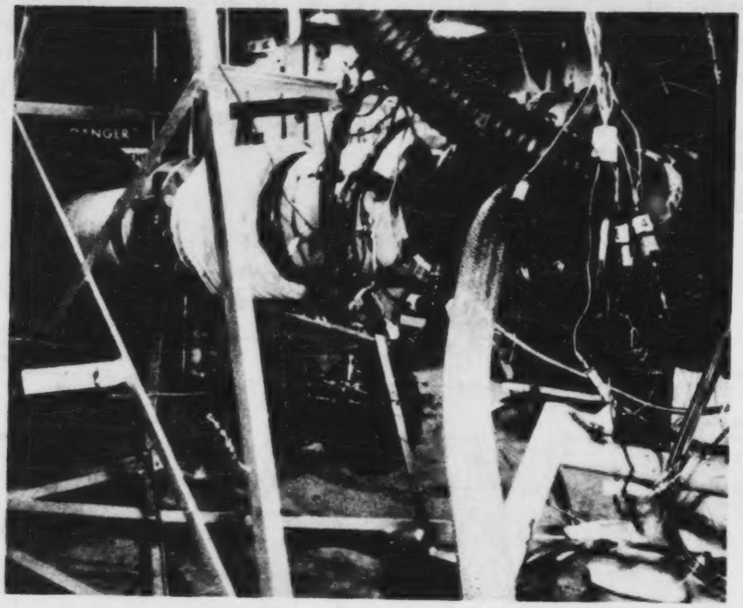


Figure 18. Combustor rig gas generator test section.

Emission Instrumentation

Exhaust gas analysis was undertaken with a Scott Model 108- Mk. III exhaust gas analysis system. The system comprises of the following instruments:

	Accuracy
Beckman Model 865-14 NDIR Analyzer for CO	1% of full scale
Beckman Model 864-23 NDIR Analyzer for CO_2	1% of full scale
Beckman Model 951H Chemiluminescence analyzer for NO, NO_x	1% of full scale
Scott Model 415 FID for Hydrocarbons	1% of full scale

Flow schematic of the gas analysis system is shown in Figure 19. Sample to the HC analyzer is maintained at temperatures of 150 ± 5°C and downstream to the other instruments at 55 ± 5°C. All additional components such as valves, solenoids, pumps etc. are also heated to the same temperatures. The system does a wet sample analysis and no desiccants, dryers or water traps are used in the system.

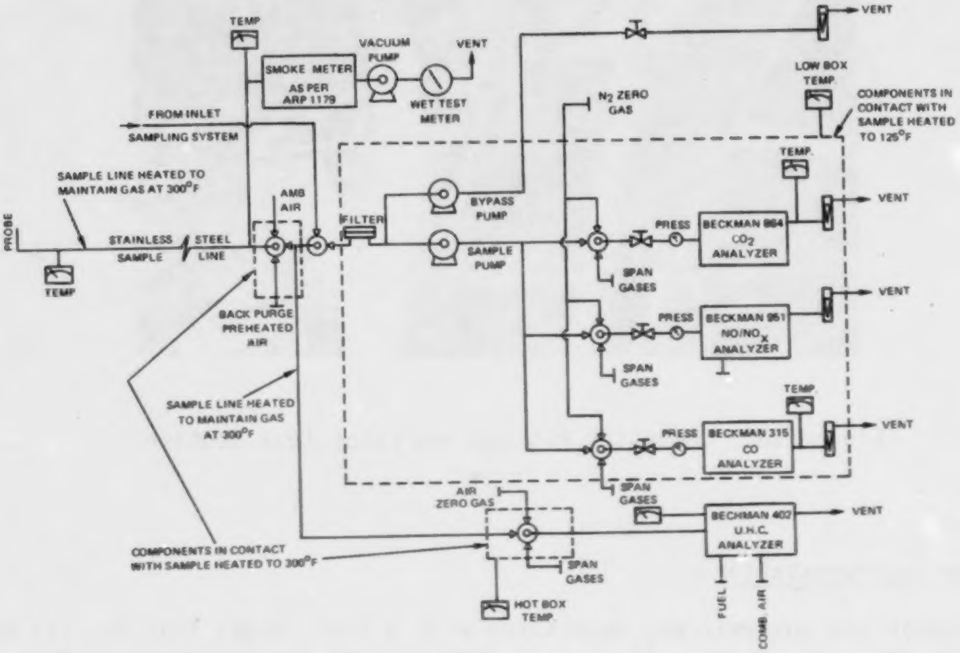

TEMP
SMOKE METER
AS PER ARP 1179
VACUUM PUMP
VENT
WET TEST METER
FROM INLET
SAMPLING SYSTEM
SAMPLE LINE HEATED TO MAINTAIN GAS AT 300°F
PROBE
STAINLESS
STEEL
SAMPLE
LINE
TEMP
AMB AIR
FILTER
BYPASS PUMP
SAMPLE PUMP
BACK PURGE PREHEATED AIR
SAMPLE LINE HEATED TO MAINTAIN GAS AT 300°F
COMPONENTS IN CONTACT WITH SAMPLE HEATED TO 300°F
VENT
LOW BOX TEMP.
COMPONENTS IN CONTACT WITH SAMPLE HEATED TO 125°F
N_2 ZERO GAS
TEMP.
PRESS
BECKMAN 864
CO_2 ANALYZER
VENT
SPAN GASES
PRESS
BECKMAN 951
NO/NO_X ANALYZER
VENT
SPAN GASES
TEMP.
PRESS
BECKMAN 315
CO ANALYZER
VENT
SPAN GASES
AIR ZERO GAS
BECKMAN 402
U.H.C. ANALYZER
VENT
SPAN GASES
HOT BOX TEMP.
FUEL
COMB. AIR

Figure 19. Exhaust emission instrumentation.

Emission measurements were made in accordance with EPA regulations Federal Register, 17 July 1973. The emission sampling probes are situated between the gas generator exhaust and the butterfly valve. A total of 12 sampling points provided for collection of representative samples. This was achieved by arranging 4 sampling probes to form a cruciform within the tailpipe as shown in Figure 19.

Equipment for analysis of engine intake air consisted of all of the exhaust emissions analyzers, plus a separate Beckman Model 400 hydrocarbon analyzer. Inlet air humidity was measured with an EG and G Cambridge Systems Model 880 dew point hygrometer with a 'Peltier' cooler and optical detector.

All calibration gases used on the exhaust emissions systems were purchased from Scott Research Labs and certified to 2% accuracy. Calibration gases for the Beckman Model 400 hydrocarbon analyzer are primary standards supplied by Matheson of Canada Limited.

TRIAL RUNS

The hardware and test instrumentation were checked out by conducting trial runs which included a series of emissions and performance tests. The tests were undertaken at conditions simulating ground idle, approach, climbout and takeoff modes. In addition, emissions mapping of the exhaust pipe was also undertaken to determine specie distribution at the exit from the gas generator.

The combustor test conditions simulating the four operating modes of the engine are shown in Table 7.

TABLE 7. PT6A-45 GAS GENERATOR TEST CONDITIONS

Operating Mode	Gas Gen. Speed N_G (RPM)	Fuel Flow Wf (pph)	HP	Remarks
Ground Idle	22,500	155	75	Run to mechanical conditions.
Approach	31,400	300	336	Run to normalized* conditions.
Climbout	37,100	600	1008	Run to normalized* conditions.
Takeoff	37,700	640	1120	Run to normalized* conditions.

* N_G (NORM) = N_G (MECH) ; Wf (NORM) = Wf (MECH)

Exit Pipe Mapping

An exhaust plane mapping was made to confirm the relative homogeneity of exhaust samples at various points within the exhaust duct of the PT6A. A single point probe was used to do diametral traverses along four circumferential planes and gaseous emissions were measured at nine positions in each plane. Tests were undertaken at combustor conditions simulating ground idle and climbout.

The emissions traverses covered two 90° sectors of the exhaust pipe. Table 8 summarizes maximum deviations in specie concentration relative to the mean for ground idle and climbout operating modes.

TABLE 8. DEVIATIONS IN SPECIE CONCENTRATIONS

		GROUND IDLE				CLIMBOUT			
		CO_2 %	HC ppm	CO ppm	NO_x ppm	CO_2 %	HC ppm	CO ppm	NO_x ppm
Avg. Concentration		2.86	161.0	410.0	31.7	4.29	-	54.2	-
Max Deviation %	+	3.85	18.01	7.32	7.32	5.62	-	3.41	-
	-	3.85	22.9	3.90	11.62	4.40	-	3.97	-

Wider specie distributions were observed with hydrocarbons and NO_x at idle then at climbout. However, reasonable CO_2 distribution which largely determines local fuel-air ratios indicated generally good mixing at both idle and climbout conditions (Figures 20 and 21).

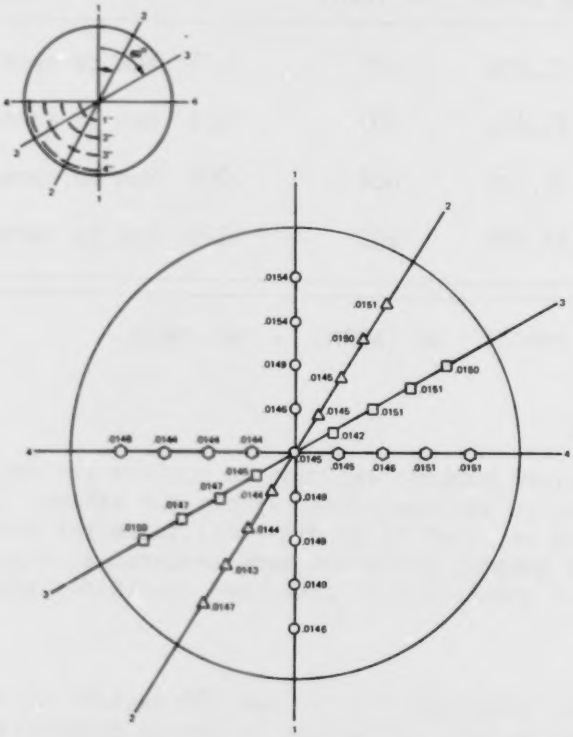


Figure 20. Fuel-air ratio distribution in exhaust pipe (PT6A-45 gas generator at idle condition).

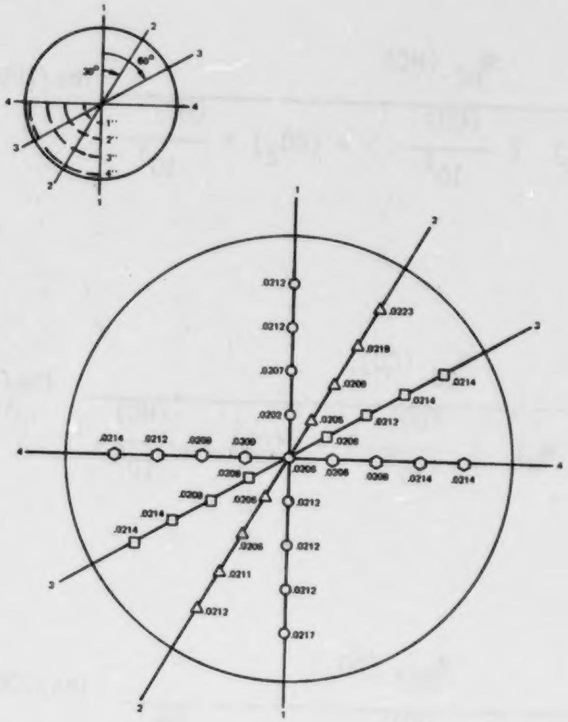

1
2
3
4
30°
60°
1"
2"
3"
4"
.0212
.0212
.0207
.0202
.0223
.0219
.0209
.0205
.0214
.0214
.0212
.0206
.0214
.0212
.0209
.0209
.0206
.0206
.0209
.0214
.0214
.0208
.0209
.0214
.0214
.0206
.0212
.0206
.0212
.0211
.0212
.0212
.0212
.0217

Figure 21. Fuel-Air ratio distribution in exhaust pipe (PT6A-45 gas generator at climbout condition).

The gas generator was then set up for performance and emission check runs. Exhaust pipe instrumentation included a ten point cruciform emission probe and a four point (T_7) temperature probe. The gas generator was run to a matrix similar to that planned for the final (Phase II) collection runs. This included five cycles at idle and approach followed by two climbout, four takeoff and again three climbout mode tests. In each case all gas generator performance as well as exhaust emission data were collected. The generator was run without any accessory loads or bleeds. Table 9 shows a summary of the gas generator data and emission indices of THC, CO, CO_2 and NO_x. The emission index is a means of expressing the emission characteristics of a combustor in relation to the fuel consumed. It is typically expressed as pounds of pollutants per thousand pounds of fuel. In addition a carbon balance check was done at each condition comparing calculated fuel-air ratio with fuel-air ratios from measured fuel and air flows. The conformity of these two parameters was within 10% indicating a representative exhaust sample. The mole fractions of THC, CO and NO_x were reduced to Emission Indices (EI) using the following relations:

$$EI_{HC} = \frac{M_{HC}\ (HC)}{10(M_C + M_H)\ \left(\frac{(CO)}{10^4}\right) + (CO_2) + \frac{(HC)}{10^4}}\ \text{lbs/1000 lb. fuel}$$

$$EI_{CO} = \frac{M_{CO}\ (CO)}{10(M_C + M_H)\ \left(\frac{(CO)}{10^4}\right) + (CO_2) + \frac{(HC)}{10^4}}\ \text{lbs/1000 lb. fuel}$$

$$EI_{NO_x} = \frac{M_{NO2}\ (NO_x)}{10(M_C + M_H)\ \left(\frac{(CO)}{10^4}\right) + (CO_2) + \frac{(HC)}{10^4}}\ \text{lbs/1000 lb. fuel}$$

where, M_{HC} = Molecular weight of Methane

M_{CO} = Molecular weight of Carbon Monoxide

M_{NO_2} = Molecular weight of Nitrogen Dioxide

M_C = Atomic weight of Carbon

M_H = Atomic weight of Hydrogen

α = Atomic Hydrogen-Carbon ratio of fuel

(HC), (CO), (NO_x) = ppm concentrations of HC, CO & NO_x

(CO_2) = % concentration of CO_2.

TABLE 9. SUMMARY OF EMISSION DATA (PHASE I)
PT6A-45 GAS GENERATOR WITH MK VI FLAME TUBE

									CARBON BALANCE							
COND	NORM.NG	MECH.WF	T1(F)	T3(F)	EI(THC)	EI(CO)	EI(NO2)	EFFY	$(F/A)_C$ *	$(F/A)_H$ +	EI(CO2)	%(CP2)	SIMULATED POWER SETTING	REMARKS	EI(CO_2)	%(CO_2)
7	22052.	154.2	80	276	4.68	25.82	3.83	.9897	.01558	.01436	3117.8	3.15	Idle		3117.8	3.15
8	31397.	308.5	83	492	0.00	4.97	7.00	.9988	.01461	.01477	3163.4	3.00	Approach		3163.4	3.00
9	21937.	154.2	86	200	4.46	26.92	4.06	.9897	.01508	.01453	3116.6	3.05	Idle		3116.6	3.05
10	31409.	307.6	84	494	0.00	4.92	6.93	.9989	.01476	.01475	3163.5	3.03	Approach		3163.5	3.03
11	22054.	154.1	83	278	4.39	25.83	3.78	.9900	.01558	.01439	3118.5	3.15	Idle		3118.5	3.15
12	31452.	306.5	80	488	0.00	4.85	6.88	.9989	.01476	.01458	3163.6	3.03	Approach		3163.6	3.03
13	22119.	155.2	81	276	4.32	25.93	3.63	.9901	.01533	.01432	3118.6	3.10	Idle		3118.6	3.10
14	31416.	307.3	81	489	0.00	4.72	7.31	.9989	.01476	.01468	3163.8	3.03	Approach		3163.8	3.03
15	22047.	154.1	81	275	4.36	26.08	3.66	.9900	.01543	.01432	3118.2	3.12	Idle		3118.2	3.12
16	31434.	307.4	77	483	0.00	5.54	6.88	.9987	.01486	.01462	3162.5	3.05	Approach		3162.5	3.05
17	37190.	613.4	75	625	0.00	1.80	9.57	.9996	.02133	.02014	3168.4	4.36	Climbout		3168.4	4.36
18	37234.	616.8	74	624	0.00	1.56	10.31	.9996	.02153	.02019	3168.8	4.40	Climbout		3168.8	4.40
19	37399.	636.6	68	616	0.00	2.44	9.32	.9994	.02104	.02060	3167.4	4.30	Take Off	T5 Limited	3167.4	4.30
20	37488.	636.4	69	681	0.00	2.47	9.35	.9994	.02079	.02055	3167.3	4.25	Take Off	T5 Limited	3167.3	4.25
21	37263.	634.3	72	620	0.00	2.44	9.16	.9994	.02104	.02071	3167.4	4.30	Take Off	T5 Limited	3167.4	4.30
22	37083.	626.7	74	623	0.00	2.72	9.16	.9994	.02104	.02056	3166.9	4.30	Take Off	T5 Limited	3166.9	4.30
23	37168.	625.6	74	621	0.00	2.34	9.32	.9995	.02104	.02052	3167.5	4.30	Take Off	T5 Limited	3167.5	4.30
24	37037.	612.1	75	624	0.00	2.77	9.32	.9994	.02105	.02108	3166.9	4.30	Climbout		3166.9	4.30
25	36868.	611.5	83	632	0.00	2.33	9.02	.9995	.02119	.02042	3167.6	4.33	Climbout		3167.6	4.33
26	36787.	605.3	84	635	0.00	2.25	9.32	.9995	.02104	.02030	3167.7	4.30	Climbout		3167.7	4.30

* $(F/A)_C$ = F/A CALCULATED FROM EMISSION DATA

+ $(F/A)_H = W_F/3600\ (W_3 + W_{cool})$

Figure 22 shows a plot of average emission indices as a function of gas generator speed. This data is fairly typical of the low emission combustor under test.

Using the emission index data at idle, approach, climbout and takeoff EPA emission parameters may be computed for the EPA defined (Federal Register July 17, 1973) landing takeoff (LTO) cycle. This results in the cycle emission parameters shown in Table 10.

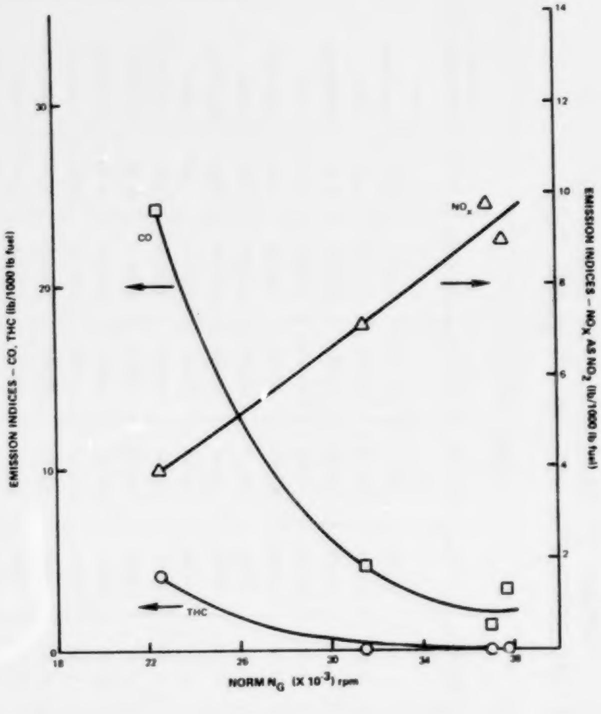


Figure 22. Emissions profiles - phase I.

TABLE 10. LTO CYCLE EMISSIONS & EPA (1979) STANDARDS

	AMBIENT		E P A P***		
	T °F	S.H.**	THC	CO	NO_x
Low Emissions Combustor PT6A-45	80	.0083	2.61	16.23	6.58*
EPA (1979) STD (P_2 Class)	59	.0063	4.9	26.8	12.9

* Not corrected for humidity

**Specific Humidity

***lbs/1000 lb-thrust hours/cycle

The gas generator was allowed to stabilize for 10 minutes at each test condition prior to collection of samples. Gaseous emissions were periodically monitored while adequate number of particulate and smoke samples were collected.

Midway through the trial program samples of the low sulfur Jet A-1 fuel were collected from the fuel system and sampled for sulfur concentration. These samples showed an average sulfur content of 0.0075 weight percent. Table 11 is a summary of test conditions and gaseous emission data obtained during Phase II collection runs with low sulfur Jet A-1 fuel.

Prior to the second series of tests, the sulfur content of Jet A-1 fuel was increased to EPA specifications by adding ditertiary butyl disulfide to the fuel tank. After addition of a known amount of the additive (1.12 gallons/1000 lbs.) the well mixed fuel in the tank was analyzed. These samples gave sulfur concentrations of 0.255 weight percent on average.

The second series of tests was similar to the first, except for the changed fuel specifications. Once again an adequate number of samples were collected after the gas generator had stabilized at the test conditions for a minimum period of ten minutes. In some cases takeoff modes could not be simulated due to T_5 temperature maximum limits. This is typical of engine operations during hot summer days (high inlet temperatures). In such cases the gas generator was run at its T_5 limit (maximum temperature limit 1580°F at the first turbine stage exit).

The engine inlet air was analyzed. It showed the following constituents:

HC : 0 (i.e. none detectable)

CO : 5.5 ppm

NO_x : 3.5 ppm

CO_2 : 0.04%

Table 12 is a summary of test conditions and gaseous emission data obtained during Phase II collection runs with high sulfur Jet A-1 fuel.

TEST PROCEDURE

Phases I and II of the contract called for the demonstration and documentation of the proper and consistent operation of the test vehicle with special emphasis on consistent mass emissions and gaseous emissions.

TABLE 11. PHASE II TESTS (LOW SULFUR FUEL)

COND	NORM Ng	MECH Wf	°F T1	°F T3	EMISSION INDICES			Efficiency	FUEL-AIR RATIO		SIMULATED POWER SETTING	REMARKS
					EI THC	EI CO	EI NO_2		$(F/A)_C$*	$(F/A)_M$+		
27	36648	612.8	74	613	0	1.46	9.80	.9997	.02168	.02048	Climbout	T_5 Limited at T.O.
28	36237	599.3	78	613	0	1.37	9.80	.9997	.02168	.02046	Climbout	
29	31285	310.3	84	491	0	4.87	6.83	.9989	.01510	.01494	Approach	
30	31457	308.9	80	489	0	4.75	6.99	.9989	.01469	.01485	Approach	
31	37653	643.6	66	619	0	2.57	9.82	.9994	.02229	.02066	Take Off	T_5 Limited
32	37132	610.8	73	619	0	2.49	9.75	.9994	.02179	.02002	Climbout	
33	22067	154.8	79	272	3.93	24.98	3.39	.9906	.01571	.01422	Idle	
34	21979	153.6	85	280	3.78	24.92	3.46	.9908	.01631	.01445	Idle	
35	21927	153.4	87	281	4.36	26.55	3.57	.9899	.01283	.01447	Idle	
36	31411	308.5	87	501	0	6.50	7.31	.9985	.01265	.01482	Approach	
37	37634	637.9	64	612	0	2.22	8.73	.9995	.02229	.02055	Take Off	T_5 Limited
38	37458	629.6	72	621	NT	NT	NT	-	-	.02056	Take Off	T_5 Limited
39	37089	601.9	71	619	NT	NT	NT	-	-	.01992	Climbout	
40	31433	298.4	69	467	NT	NT	NT	-	-	.01425	Approach	
41	22293	153.3	69	265	NT	NT	NT	-	-	.01407	Idle	

* $(F/A)_C$ = F/A calculated from emission data

NT = Not Taken

+ $(F/A)_M = W_F/3600\ (W_3 + W_{cool})$

TABLE 12. PHASE II TESTS (HIGH SULFUR FUEL)

COND	NORM Ng	MECH Wf	°F T1	°F T3	EMISSION INDICES EI THC	EI CO	EI NO_2	Efficiency	CARBON BALANCE $(F/A)_C$*	$(F/A)_M$+	SIMULATED POWER SETTING	REMARKS
42	37682	637.4	60	608	0	2.92	8.66	.9993	.02230	.02042	Take Off	T_5 Limited at T.O.
43	37041	599.6	64	600	0	3.40	8.46	.9992	.02145	.01968	Climbout	
44	31371	300.2	68	466	0	7.59	5.16	.9982	.01290	.01430	Approach	Diaphragm failure in sample pump
45	22193	154.9	73	266	6.09	27.41	3.13	.9881	.01282	.01420	Idle	
46	31330	303.0	71	469	0	6.53	6.24	.9985	.01289	.01449	Approach	
47	37548	646.0	64	611	0	2.48	9.46	.9994	.02229	.02068	Take Off	T_5 Limited
48	37042	609.7	68	609	0	2.75	8.95	.9994	.02154	.01991	Climbout	
49	22188	154.9	74	266	4.85	27.68	3.36	.9892	.01560	.01406	Idle	
50	32148	314.8	94	531	NT	NT	NT	-	-	.01454	Approach	
51	21808	164.0	93	286	NT	NT	NT	-	-	.01638	Idle	
52	37061	608.9	77	624	NT	NT	NT	-	-	.02026	Take Off	T_5 Limited
53	34963	475.7	92	600	NT	NT	NT	-	-	.01786	Approach	
54	33071	377.4	90	552	NT	NT	NT	-	-	.01626	Approach	
55	31301	297.4	76	474	NT	NT	NT	-	-	.01459	Idle	

* $(F/A)_C$ = F/A calculated from emissions data

+ $(F/A)_M = W_F/3600\ (W_3 + W_{cool})$

NT = Not Taken

Phase I

Using a PT6A-45 gas generator and a typical sampling rake (see Figure 26) EPA smoke and gaseous emissions data were taken. In addition to this data, a tailpipe mapping was performed with respect to engine emissions. The data shows that a) the engine exhaust is reasonably uniform in terms of gaseous emissions, b) it is a low emissions gas turbine and c) it was operated in a predictable and repeatable fashion.

Smoke data was taken using an EPA type smoke meter (Figure 23) that was designed and built in conformance with Federal Register Vol. 38, No. 136, July 17, 1973 and Aerospace Recommended Practice 1179 (5/4/70). The samples, which consisted of a series of stained filters, were analyzed using a Photovolt model No. 670 reflectance meter. Replicate samples of smoke data were taken so that smoke data from each of four power points was taken 15 times. The filter type used was Whatman filter paper #4.

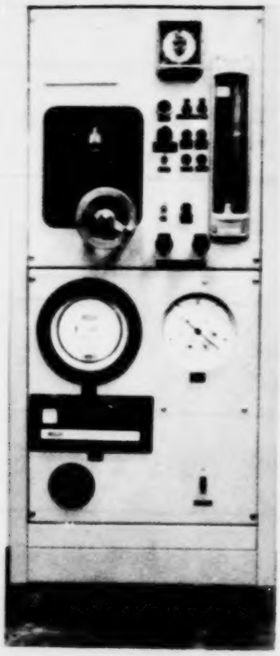


Figure 23. SAE/EPA smoke meter.

Mass emission data were taken using the same smoke meter described above. In this test a hydrophobic Nuclepore, 40 mm diameter filter was used. Each filter was preconditioned and preweighed several times to insure equilibrium in humidity-temperature controlled atmosphere. The device used to make these filter weight measurements was a Perkin-Elmer Model AD-2 electrobalance located in a room where temperature was 69°F and relative humidity was 50%. After the particulate material was collected on these filters by allowing a 0.9 to 2.1 m^3 of the exhaust to pass through, they were returned to the same room where they were allowed to equilibrate for several days then weighed by a similar process. Replicate filter samples at each of four power points on low sulfur fuel only were taken resulting in several loaded filters for each power setting. Filter blanks were taken to monitor the entire process.

Tailpipe mapping was performed on the engine using a traversing rake. The rake was allowed to traverse a diameter of the tailpipe taking emissions data at 9 points which represented centroids of equal areas. This process was repeated several times with the diameter rotated 30°, 60° and 90° from the first. The emission measurements, taken in this sequence, were NO_x, CO, CO_2 and total hydrocarbons.

Phase II

During this phase of testing particulate material for numerous chemical analyses were taken. In addition a sulfur collection train was used to collect gaseous and aerosol sulfur products in the engine exhaust stream. Samples were obtained from the engine inlet to ascertain the quality of the inlet air used during these tests and eliminate a possible source of error in the final results.

Using a sampling system comprised of a linear rake and plenum chamber, Roots model 3514J vacuum blower system, fixed orifice flow metering devices and filter holding console (holding five 293 mm diameter filters), particulate material was collected for various chemical analyses. Mitex (10 micron) and glass fiber filters were exposed to engine exhaust to collect particulate material in sufficient quantity for the chemical tests required. While the sampling was being done the gas temperature in each of the filter holders were monitored. Temperature and pressure data necessary to make flow calculations with the fixed orifice gas metering tubes was also taken.

Previous tests showed that serious degradation occurred when temperatures at the filter were above 160°F. During the testing, unacceptably high filter temperatures occurred but were resolved using two techniques. One method was to throttle the flow so that the gases had time to cool before entering the filter holder. The other method was to use longer water cooled heat exchangers. Using a combination of both techniques the filter temperatures varied between 100 and 160°F, assuring minimum sample degradation.

Because it was impossible to control temperature consistently the exhaust gas temperature at times was over-cooled, dropping the temperature below the dew point. This resulted in moisture condensing on the filter material causing unusually high pressure drops. The Roots pump was designed to operate efficiently at up to 4 inches Hg vacuum. Serious damage would occur if a vacuum of 8 inches Hg was reached. Bypass air was allowed to enter the pump to prevent this situation. Particulate loading coupled with the condensed moisture proved to be a serious obstacle in collecting what was thought to be a reasonable weight of particulate sample. This problem was somewhat mitigated by extending the sampling times to acquire more particulate material.

Sulfur oxide samples were collected by drawing the exhaust gases through a series of bubblers to extract the sulfur oxides from the exhaust stream. These bubblers form a gas sampling train similar to the one described in method 8 of the Federal Register, June 8, 1976. In this sampling train fritted bubblers are used instead of the impingers described and the filter (and filter holder) was omitted. The test is set up so that sulfur oxides in the form of SO_3 can be differentiated from SO_2. The data was taken using four power settings and two fuels (low and high sulfur).

An attempt was made to evaluate a filter system using a packed bed of gas chromatographic column material. Four columns of Chromsorb 102 (Figure 14) were used to collect organic material in engine exhaust. A sample line from the sample plenum was used to conduct exhaust gases to the packed column. Sample flow through the bed was extremely slow so that relatively small total flows were realized. The relatively slow flow rate was due primarily to the fine mesh of the Chromsorb 102 used as the adsorbent. Samples were obtained of two engine power settings using both high and low sulfur fuels.

All samples (filter, packed column and liquid) were packed in an ice chest filled with dry ice immediately after they were taken. The samples were kept continuously in this condition throughout the test in Canada, while they were shipped back to the analytical laboratory in East Hartford, and until they were eventually processed for analysis.

SAMPLE IDENTIFICATION

Due to the large number of filters that were processed in the course of the fulfillment of the EPA contract, it was necessary to initiate an identification system. From Table 4, it can be seen that a minimum of 66 Mitex, 12 glass fiber and 20 Nuclepore filters were used. It was necessary to expose filters to engine exhaust while the engine was at 4 power settings. In addition, fuels with two sulfur concentrations were used. In some cases replicate samples were taken. These samples were identified using the following letter/number scheme:

I. Specific Analysis (or Disposition)

1. HPLC/UV = LC/UV
2. Phenols and Nitrosamines = P/N
3. Infrared = IR
4. Nuclear Magnetic Resonance = NMR
5. Gas Chromat./Mass Spec. = GC/MS
6. Boiling Point Analysis = BP

7. Total Organic (via GC) = T/ORG
8. Special for EPA (X-Ray) = EPA
9. Elemental Analysis = EL
10. Mass Emissions = ME
11. Sulfur Analysis = S
12. Proton Activation Analysis = PAA

II. Power Points:

1. = Idle
2. = Approach
3. = Climb
4. = Takeoff

III. Fuel: A = Low sulfur
B = Hi sulfur

IV. Replicate Samples

First Sample = #1
Second Sample = #2
Third Sample = #3

Using this system the designation of filters for the HPLC/UV analysis using both fuels, all power points and in some cases taking two replicate samples were as follows:

A. HPLC/UV

1) LC/UV-1-A #1
2) LC/UV-1-A #2
3) LC/UV-2-A #1
4) LC/UV-2-A #2

5) LC/UV-3-A #1
6) LC/UV-3-A #2
7) LC/UV-4-A #1
8) LC/UV-4-A #2
9) LC/UV-1-B
10) LC/UV-2-B
11) LC/UV-3-B
12) LC/UV-4-B

D. Nuclear Magnetic Resonance
1) NMR - 1 -A
2) NMR - 3 -A
3) NMR - 1 -B
4) NMR - 3 -B

Similarly:

B. Phenols/Nitrosamines
1) P/N - 1 -A
2) P/N - 3 -A

C. Infrared
1) IR - 1 -A
2) IR - 3 -A
3) IR - 1 -B
4) IR - 3 -B

H. Special EPA Filters
1) EPA - 1 -A
2) EPA - 2 -A
3) EPA - 3 -A
4) EPA - 4 -A
5) EPA - 1 -B
6) EPA - 2 -
7) EPA - 3 -B
8) EPA - 4 -B

E. G/C - Mass Spec.
1) GC/MS - 1 -A #1
2) GC/MS - 1 -A #2
3) GC/MS - 2 -A #1
4) GC/MS - 2 -A #2
5) GC/MS - 3 -A #1
6) GC/MS - 3 -A #2
7) GC/MS - 4 -A #1
8) GC/MS - 4 -A #2
9) GC/MS - 1 -B #1
10) GC/MS - 1 -B #2
11) GC/MS - 2 -B #1
12) GC/MS - 2 -B #2
13) GC/MS - 3 -B #1
14) GC/MS - 3 -B #2
15) GC/MS - 4 -B #1
16) GC/MS - 4 -B #2

F. Boiling Point Anal.
1) BP - 1 -A
2) BP - 2 -A
3) BP - 3 -A
4) BP - 4 -A
5) BP - 1 -B
6) BP - 2 -B
7) BP - 3 -B
8) BP - 4 -B

G. Total Organic (via GC)
1) T-ORG - 1 -A #1
2) T-ORG - 1 -A #2
3) T-ORG - 1 -A #1
4) T-ORG - 2 -A #2
5) T-ORG - 3 -A #1
6) T-ORG - 3 -A #2
7) T-ORG - 4 -A #1
8) T-ORG - 4 -A #2
9) T-ORG - 1 -B
10) T-ORG - 2 -B
11) T-ORG - 3 -B
12) T-ORG - 4 -B

I. Elemental Analysis
1) EL - 1 -A #1B
2) EL - 1 -A #2
3) EL - 2 -A #1
4) EL - 2 -A #2
5) EL - 3 -A #1
6) EL - 3 -A #2
7) EL - 4 -A #1
8) EL - 4 -A #2
9) EL - 1 -B
10) EL - 2 -B
11) EL - 3 -B
12) EL - 4 -B

J. Mass Emissions
1) ME - 1 -A #1
2) ME - 1 -A #2
3) ME - 1 -A #3
4) ME - 2 -A #1
5) ME - 2 -A #2
6) ME - 2 -A #3
7) ME - 3 -A #1
8) ME - 3 -A #2
9) ME - 3 -A #3
10) ME - 4 -A #1
11) ME - 4 -A #2
12) ME - 4 -A #3

K. Proton Activation Analysis
1) PAA - 1 -A #1
2) PAA - 1 -A #2
3) PAA - 2 -A #1
4) PAA - 2 -A #2
5) PAA - 3 -A #1
6) PAA - 3 -A #2
7) PAA - 4 -A #1
8) PAA - 4 -A #2
9) PAA - 1 -B
10) PAA - 2 -B
11) PAA - 3 -B
12) PAA - 4 -B

MASS EMISSIONS MEASUREMENT TECHNOLOGY

Mass emissions measurements have historically been a subject of question and controversy due to a number of variables involved with filter preparation, sampling technique, and post test weight analysis. Over the past several years, P&WA has improved its methods in mass emissions measurement to a point where the resultant data can be considered both repeatable and sufficiently accurate to be useful as a tool in monitoring emissions in gas turbine engines.

Filters

A number of filter materials have been examined as possible candidates for particulate collection. Among these have been Mitex (teflon), standard Millipore (mixed esters of cellulose), PVC (polyvinyl chloride), Metricel (mixed esters of cellulose) and Nuclepore (polycarbonate plastic). Some of these filters have had a problem with water absorption and desorption. There have also been problems with temperature, mechanical integrity, trapping efficiency and actual mass of the filter (since a heavier filter will absorb more water than a lighter one of the same material).

Nuclepore filters were ordered from Nuclepore Corporation in the non-standard 40 mm diameter used. The filters were therefore clean cut without frayed edges and were handled only under clean room conditions. Each filter was numbered and set in a 47 mm petri dish half to equilibrate in a temperature and humidity controlled room (20°C, 50% RH) for a period of 72 hours. After equilibration, each filter were passed several times over a static discharge source and then placed on the weighing pan of a Perkin Elmer AD-2 electrobalance.

A minimum of three pretest and three post-test weighings were made for each filter. Additional weighings were taken as necessary to insure that filters were equilibrated and data were repeatable. The post-test filters were set in petri dish halves as in the pretest preparation and were allowed to equilibrate for a minimum of 72 hours.

Balance

Experience has shown that mechanical balances designed for microgram weighing are not suitable for mass emissions filter analysis. The weighings are not stable and repeatable when attempted on a marble table in an industrial setting. Vibration and air movement caused by temperature and humidity control equipment make it unlikely that they would be suitable in any setting.

The Perkin-Elmer AD-2 electrobalance was chosen for mass emissions testing because it has resolution to 0.1 microgram and is electronically dampened so that it maintains a high level of stability. Calibration was checked before, during and after each weighing period using a Class S weight set.

Mass Emissions Testing

Mass emissions were collected using a P&WA built SAE/EPA smoke meter. P&WA Canada's multi-point emissions rake was used to deliver the sample to a 1/4" stainless steel line heated to 150°C. Immediately after testing each filter was sealed in a petri dish and returned to the laboratory for equilibration. The mass of the accumulated particulate matter ranged from approximately 250 ug to 1000 ug. Sampling time ranged from 3 to 6 minutes per filter and the collected volume ranged approximately from 0.9 to 2.1 m^3.

Mass emissions measurements from Phase I are shown in Table 13. Five gas generator tests, each at four simulated power settings were performed. Samples were taken in triplicate where possible. The mechanical fuel-air ratio calculated from actual fuel and air flows are in parentheses in Table 13.

Mass emissions measurements from Phase II are shown in Table 14. Two gas generator tests, each at four simulated power settings were performed. Again, samples were taken in triplicate where possible and the mechanical fuel-air ratio is given in parentheses.

TABLE 13. MASS EMISSIONS MEASUREMENT - PHASE I (mg/m^3)

Test Number	1	$(F/A)_M$	2	$(F/A)_M$	3	$(F/A)_M$	4	$(F/A)_M$	5	$(F/A)_M$
Idle	3.320 2.790	(.01436)	3.178 2.896 3.567	(.01453)	2.825 3.108 3.037	(.01439)	3.108 2.790 3.289	(.01432)	2.684 3.320	(.01432)
Approach	4.732 4.520 4.372	(.01477)	4.874 4.566 4.662	(.01475)	4.909 4.308 4.556	(.01458)	4.379 4.238 4.308	(.01468)	4.874 4.414 4.485	(.01462)
Climb	7.063 7.416 7.310	(.02014)	6.922 6.886 6.745	(.02019)	7.310 7.381 7.204	(.02018)	7.275 7.169 6.922	(.02042)	6.675 6.321 6.569	(.02030)
Takeoff	7.805 8.123 7.840	(.02060)	8.158 7.522 7.805	(.02055)	7.310 7.875 8.158	(.02071)	7.981 6.922 7416	(.02056)	7.310 7.734 8.087	(.02052

TABLE 14. MASS EMISSIONS MEASUREMENT - PHASE II (mg/m^3)

Test Number	1	$(F/A)_M$	2	$(F/A)_M$
Idle	2.418 2.110	(.01445)	2.036 1.903 1.940	(.01447)
Approach	3.217 3.143 3.098	(.01485)	3.945 3.744	(.01482)
Climb	7.079 7.806 3.098	(.02046)	7.787 3.744	(.01482)
Take-Off	8.478 7.946	(.02066)	9.327 9.523	(.02055)
Condition No. 53* & Condition No. 54*	6.487 6.609 6.635	(.01790)	5.629 5.644 5.785	(.01630)

*Between approach and climb power levels.

Figure 24 shows mass emissions from Phase I and Phase II as a function of mechanical F/A. Two additional power settings (conditions nos. 53 and 54) were run between approach and climb to help define the center of this curve. The data forms a tight set of points about the curve and is considered representative of the mass emissions of the PT6-A. The engine is seen to be operating in a repeatable manner.

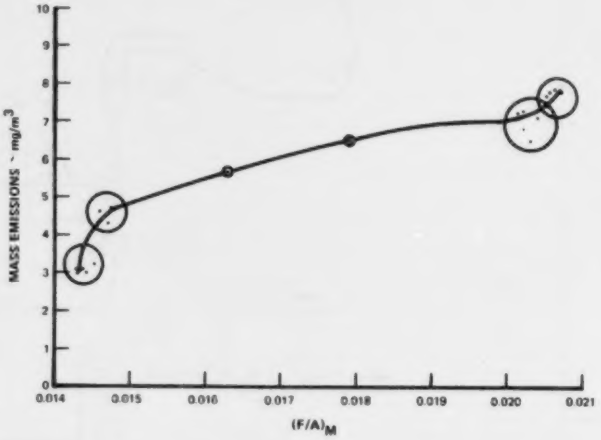


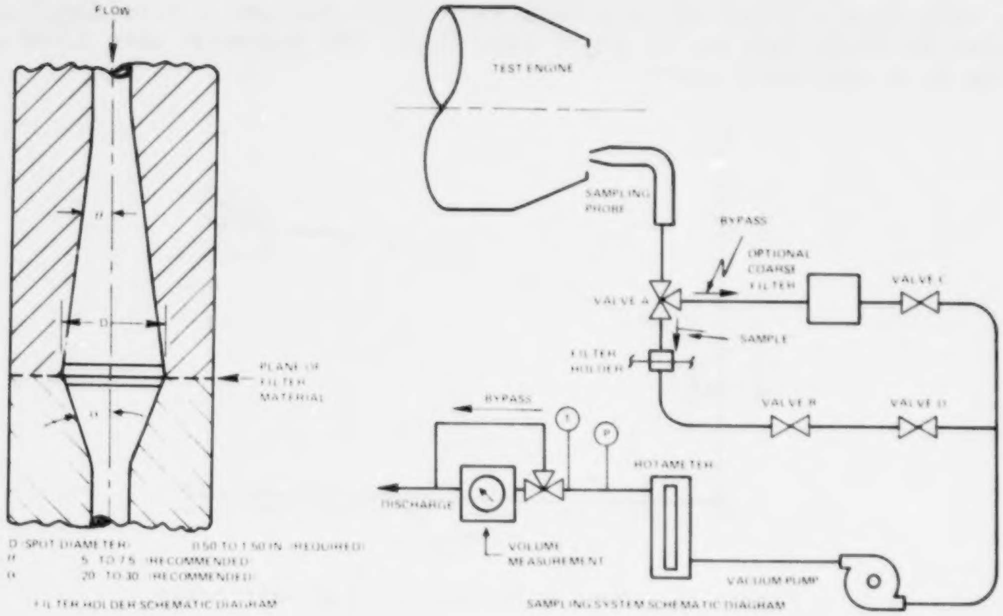
Figure 24. Mass emissions vs. fuel-air ratio.

SMOKE MEASUREMENT METHODOLOGY

An SAE/EPA smoke measurement system designed and built by P&WA in conformance with CFR 40, Number 87 Part II which appears in the Federal Register, Volume 38, Number 136, July 17, 1973 was used for the measurement of smoke (See Figures 23 and 25). Samples were extracted from the exhaust of the PT6-A using an emission sampling rake shown in Figure 26 and a 1/4-inch stainless steel line maintained at 150°C.

Five gas generator engine tests, each at four simulated power settings (idle, approach, climb and takeoff) were conducted to define smoke emissions levels throughout the engines operating range. The simulated power setting for take-off was T_5 (turbine exhaust temperature) limited and in each of the five engine tests the highest power setting obtainable within the T_5 limit was considered to be takeoff.

The smoke measuring system is a semiautomatic device which incorporates a number of features to permit the recording of smoke data with precision and ease of operation. The instrument features a timer-controlled, solenoid activated main sampling valve (Valve A, Figure 25) having closed "sample" and "bypass" positions. This system permits close control of the sample size over relatively short sampling periods. In addition, the timing system operates a bypass system around a positive displacement volume measurement meter to insure that the meter is in the circuit only when a sample is being collected, or during the leak-check mode. Automatic temperature control of the filter housing is included. The silicon-rubber filter holders have support screens for each of the filter holders.


FLOW
β
D
PLANE OF FILTER MATERIAL
α
D (SPOT DIAMETER) 0.50 TO 1.50 IN. (REQUIRED)
β 5° TO 7.5° (RECOMMENDED)
α 20° TO 30° (RECOMMENDED)
TEST ENGINE
SAMPLING PROBE
BYPASS
OPTIONAL COARSE FILTER
VALVE A
VALVE C
SAMPLE
FILTER HOLDER
BYPASS
T
P
VALVE B
VALVE D
ROTAMETER
DISCHARGE
VOLUME MEASUREMENT
VACUUM PUMP

FILTER HOLDER SCHEMATIC DIAGRAM

SAMPLING SYSTEM SCHEMATIC DIAGRAM

Figure 25. Schematic diagram of smoke meter.

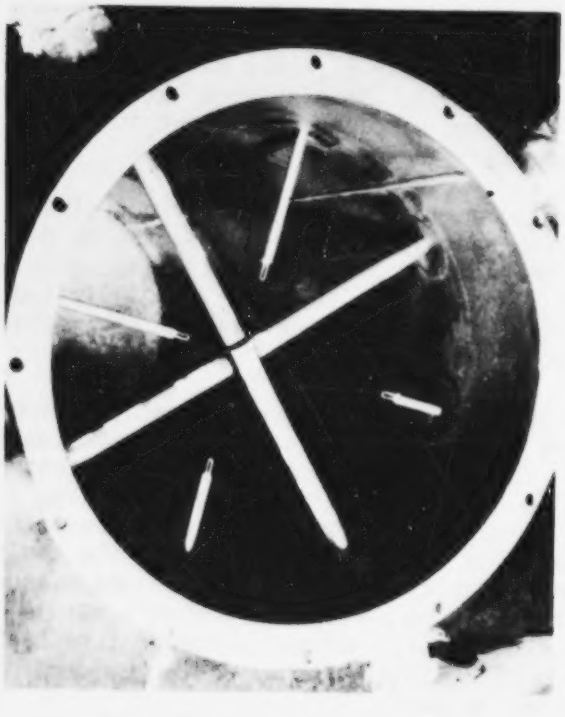


Figure 26. PT6 emission sampling rake.

The filter holder assembly was constructed with a one-inch diameter spot size, a diffusion angle of 7.25 degrees, and a converging angle of 27.5 degrees.

A Photovolt Model 670 with a Y type search unit conforming to American National Standard ASA Ph 2.17-1977 "Optical Reflection Measurements" was used to determine the reflectance of the clean and stained filters. A set of Hunter Laboratory reflectance plaques, traceable to the National Bureau of Standards, was used to calibrate the reflectance meter. A computer program was used to calculate W/A (mass/area) and smoke number for each filter.

Conclusions

Table 15 shows the results of five smoke tests at each of the four power settings. Samples were taken in triplicate and the mechanical fuel/air ratio is given as $(F/A)_M$. Smoke numbers for idle averaged 18.2, for approach 25.9, for climb 37.2, and for take-off 43.0.

TABLE 15. SAE/EPA SMOKE NUMBERS

Test Number	1	$(F/A)_M$	2	$(F/A)_M$	3	$(F/A)_M$	4	$(F/A)_M$	5	$(F/A)_M$
Idle	17.7 17.2 17.9	(.01436)	18.1 19.4 17.5	(.01453)	17.6 18.9 18.6	(.01439)	19.1 17.6 17.5	(.01432)	18.7 19.0 18.2	(.01432
Approach	26.7 24.3 25.1	(.01477)	25.4 24.8 24.7	(.01475)	25.5 26.7 25.8	(.01458)	26.3 27.6 24.7	(.01468)	26.5 26.6 27.1	(.01462)
Climb	43.2 40.4 36.5	(.02014)	39.4 38.7 36.6	(.02019)	38.0 37.7 36.2	(.02018)	37.9 38.3 35.5	(.02042)	35.3 33.1 31.7	(.02030)
Takeoff	50.8 47.3 39.6	(.02060)	48.2 47.1 42.0	(.02055)	46.9 42.9 42.2	(.02071)	40.5 39.6 36.2	(.02056)	42.5 38.2 40.5	(.02052)

Figure 27 plots average smoke number as a function of average $(F/A)_M$ and Figure 28 shows the relationship between average particulate mass emissions and average smoke number.

The smoke numbers are seen to be essentially repeatable with power setting. Some difficulty was encountered in simulating takeoffs due to the T_5 temperature limit encountered when ambient temperatures were high.

The data of Figure 27 is considered representative of this engine's smoke emissions. The linearity of Figure 27 show a consistent and linear relationship between smoke number and mass emissions and would be useful in estimating mass emissions from smoke number for this engine.

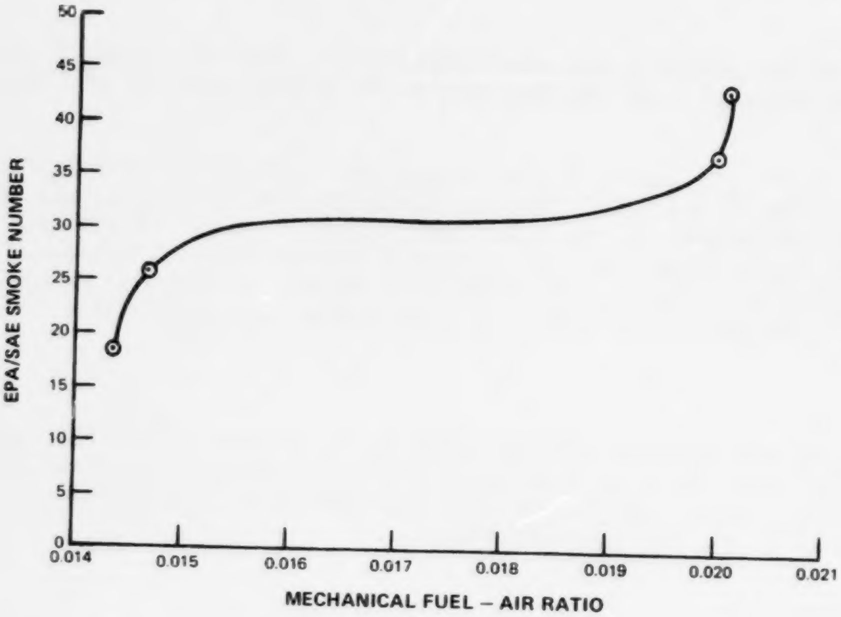


Figure 27. Average smoke numbers as function of average $(F/A)_M$.

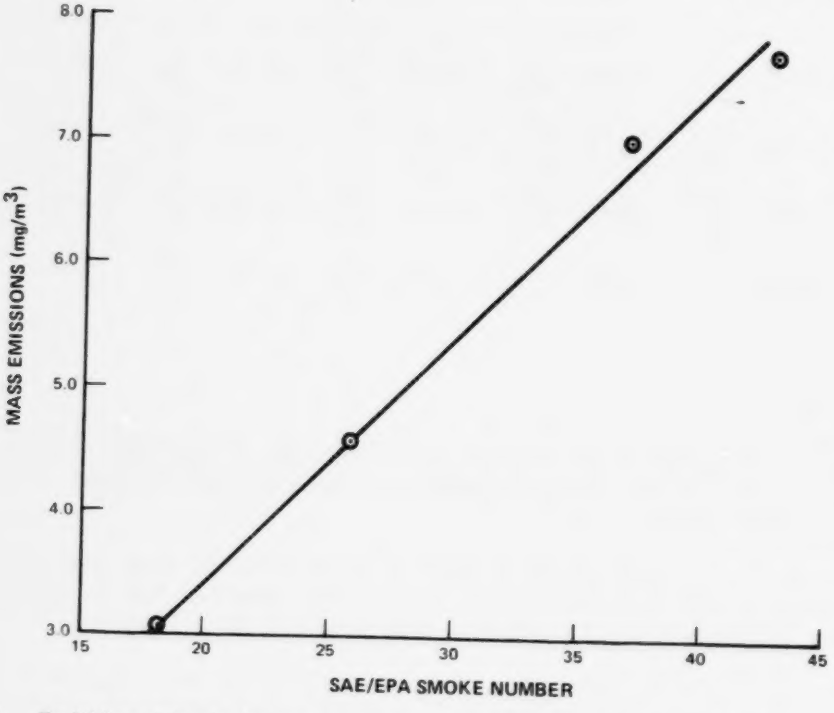


Figure 28. Reltionship between average particulate mass emissions and average smoke number.

ANALYTICAL PROCEDURES

Sample Treatment

In preparation for this work, a detailed computer literature search of both NTIS and the American Chemical Society files was conducted for information regarding the analysis of polynuclear aromatic compounds and nitrosamines.

The teflon filters obtained for chemical analysis were removed from the filter holder using forceps and gloves, folded, and placed in wide mouth 250 ml capacity polyethylene screw cap bottles. These bottles were stored immediately in a dark container kept cold with dry ice. These conditions were maintained until actual extraction of the filters was carried out.

All samples, except those for nitrosamine and phenol analyses, were extracted with appropriate solvents using a Soxhlet extractor. The apparatus consisted of a 250 ml round bottom flask containing 150 ml of solvent and the Soxhlet extractor containing the folded filter. Each extraction process was continued for a period of at least 12 hours. General references (10, 24, 28, 29, 31) suggest that this should be a reasonable time to achieve essentially complete extraction. The solvents used were as follows:

NMR analysis - deuterated chloroform
Total Organics, GC/MS, HPLC, UV, BP - hexane
Infrared - Carbon disulfide

After extraction was completed, the sample was concentrated by careful evaporation of the solvent to a final volume of 1 ml.

The choice of hexane as the usual solvent was based on high performance liquid chromatographic analyses of various solvents after concentration of impurities in the solvents. Many of these solvents, even after redistillation, still showed a concentration of impurities which would interfere in the analyses. Solvents considered were benzene, chloroform, methylene chloride, cyclohexane and hexane. The hexane used in the work was triply distilled in glass hexane obtained from Burdick and Jackson Laboratories.

The samples to be analyzed for nitrosamines and phenols were treated with phosphoric acid and extracted manually with methylene chloride and diisopropyl ether respectively in accordance with the procedure described in EPA-650/2-75/056.

The Chromosorb* 102 (a styrene - divinylbenzene polymeric material) packed filter bed material used to explore the general magnitude of the total organic emissions (gaseous and particulate) was put into a clean teflon filter and extracted by the Soxhlet method. The extracting solvent was 150 ml of hexane.

*Johns-Manville Products Corp. Celite Division, Manville, N.J.

Benzo (a) Pyrene and Sulfur Standards

Prior to a trial analyses of engine samples, it was considered desirable to analyze known samples of a polynuclear aromatic hydrocarbon to establish the sensitivity of the instrument for the substance and the linearity of the response. Benzo (a) pyrene was chosen as a representative compound for this work because of its previous use by others as a reference material and because of its possible presence in exhaust gases. Samples were exchanged with the EPA and good agreement was obtained after correction of results for purity of BAP. BAP, as commercially available, to us had up to 30% impurities. A similar program of comparison with the EPA was carried out for sulfur analyses (as sulfate) with good agreement down to the level of sensitivity of the method (ASTM D-3226-73T).

Organic Analyses

The samples collected were subjected to three basic types of analyses to characterize and semi-quantify the organic content. The total organic measurements established the magnitude of organic matter in the adsorbent and included aliphatic compounds, aromatic compounds and polycyclic organic matter. These species may or may not be oxygenated or other derivatives. The high performance liquid chromatographic analyses were used to determine the relative amounts of aromatic compounds (one or two fused rings) and polynuclear aromatic compounds. These also could include hetero atoms. The gas chromatograph-mass spectrometer analyses specifically determined individual PAH and PNA compounds.

Finally, to establish the relative amounts of organic matter adsorbed on the particulate matter and the total amount emitted by the gas generator, a packed bed filter study was carried out.

Total Organics

Samples were collected at four engine power settings using both a high sulfur and a low sulfur fuel. Duplicate samples were taken using the low sulfur fuel. These 12 samples were collected and extracted as described earlier.

Analysis was carried out using a Hewlett-Packard Model 7620A gas chromatograph with a flame ionization detector. (A photoionization detector produced by HNU, Inc., Newton, Massachusetts was reported to give much greater sensitivity for aromatic hydrocarbons but was found to develop leaks at elevated temperatures. Therefore we found it to be unusable for our purposes.)

A valve was added to permit special backflushing. The sample was introduced into the chromatograph and after a period of time, the valve was switched to reverse the flow. The lower molecular weight components including the solvent hexane passed through the column into the detector while the heavier molecules remained on the column. Upon reversing the flow the heavier components were flushed from the column into the detector giving an indication of the total amount of heavier molecules. The column used was a 6' x 1/8" OD stainless steel column packed with 10% UC-W98 (silicone gum) on 80-100 mesh Diatoport S (acid washed and silanized diatomaceous earth). The column was maintained at 190°C, the detector at 250°C and the injection port at 200°C. The carrier gas, nitrogen was set at 60 psig to give a flow of 41 ml/min. For the flame, hydrogen pressure was set at 16 psig and the air was set at 48 psig. The valve was switched after about four minutes. The sample injected was 1 ul of a total hexane extraction that was concentrated to 1 ml.

The instrument was calibrated using a) a composite sample of 16 polynuclears as shown in Table 19 plus coronene (6 fused rings) and triphenylene (4 fused rings); b) benzo (a) pyrene and c) several known compounds containing two fused rings. In the case of the composite sample, all components except fluorene were on the column when the flow was reversed. The two fused ring components and fluorene were eluted before the flow was reversed.

Table 16 gives the calibration data for these standards and Table 17 gives the results for the analyses of the 12 samples in terms of retention times and responses. The peaks shown eluted after the main hexane solvent peak.

TABLE 16. TOTAL ORGANICS CALIBRATION

Standard	Retention Time, Min	Response/ng	
		Peak Height -	Peak Area
Composite Sample, *150 ng		**	17.08
Fluorene, 10 ng	3.3	124.2	-
Naphthalene, 25 ng		0.8	324
Biphenyl, 30 ng	1.55	222.9	-
Acenaphthene, 20 ng		2.35	138.4
Methoxynaphthalene, 25 ng		2.00	94.7
Benzophenone, 25 ng		3.55	60.8
Benzo (a) pyrene, 108 ng		**	16.58

*10ng of each component, 150ng total plus 10ng fluorene

**Backflushed out. If the flow was reversed between 3.8-4 minutes, the composite was eluted at a retention time of 6.5-7 minutes.

TABLE 17. TOTAL ORGANICS ANALYSIS

Sample	Retention Time, Min.	Response	
		Peak Height	Peak Area
1A No. 1	1.25	420	-
	1.35	120	-
	1.7	372	-
	2.05	116	-
	2.45	1212	-
	3.00	92	-
	3.6	524	-
	6.55*	5952	10679
1A No. 2	2.55	1064	-
	3.7	400	-
	6.8*	7008	12578
2A No. 1	0.9	14720	-
	1.3	400	-
	1.6	208	-
	2.1	448	-
	3.3	80	-
	4.15	304	-
	6.85*	11152	13672
2A No. 2	1.38	176	-
	1.75	294	-
	2.15	164	-
	2.5	1868	-
	3.1	256	-
	3.7	1604	-
	7.2*	7080	14692
3A No. 1	2.0	92	-
	2.25	T	-
	3.2	25	-
	3.95	178	-
	7.15*	19440	25468

(Continued)

*After flow reversed

TABLE 17 (Continued)

Sample	Retention Time, Min.	Response	
		Peak Height	Peak Area
3A No. 2	2.1	232	-
	4.2	242	-
	7.05*	4390	8543
4A No. 1	2.05	220	-
	4.05	180	-
	6.65*	15040	22544
4A No. 2	1.0	T	-
	1.1	T	-
	1.3	1344	-
	1.5	320	-
	1.7	1792	-
	2.1	1093	-
	2.45	1056	-
	2.7	200	-
	3.4	120	-
	4.1	280	-
	7.1*	9312	13010
4A No. 3	1.0	584	-
	1.4	1756	-
	1.55	360	-
	1.73	1120	-
	2.15	240	-
	2.5	3484	-
	3.65	840	-
	6.5*	5748	11201
1B	0.8	784	-
	1.15	424	-
	1.35	T	-
	1.75	504	-
	2.00	127	-
	2.35	174	-
	2.7	72	-
	3.6	88	-
	6.4*	7438	12302

(Continued)

*After flow reversed

TABLE 17 (Continued)

Sample	Retention Time, Min.	Response Peak Height	Response Peak Area
2B	0.8	20704	-
	1.2	1356	-
	1.65	120	-
	2.0	70	-
	2.4	103	-
	3.25	38	-
	3.95	23	-
	6.35*	11984	16473
3B	1.2	1248	-
	1.6	108	-
	1.8	T	-
	2.45	142	-
	3.3	T	-
	4.15	96	-
	7.4*	8824	12345
4B	0.8	36768	-
	1.2	2136	-
	1.65	222	-
	1.75	T	-
	2.00	70	-
	2.4	732	-
	2.75	66	-
	3.3	76	-
	6.7*	38080	31015

*After flow reversed

In order to establish the total organic content which includes all organic species containing C-C and C-H bonds, the responses must be converted to nanograms of material. For this purpose, the sensitivities of the knowns were used where available or estimated from sensitivities of substances with similar retention times. For the large peak eluting after the flow was reversed, the sensitivity of benzo (a) pyrene (which is very close to that of the composite sample) was used. These results are given in Table 18. A range from 14.4 to 70.5 ug/m^3 are shown in the twelve samples. Most of the organic matter (92.2 - 99.6%) is in the composite peak after the flow is reversed. No trends are apparent as a function of power setting or fuel used. As will be shown later (See section on Packed Bed Filter Studies), a few exploratory samples collected on Chromosorb 102 showed that the organic matter on the particulates represent a very small percentage of the total (0.03 - 0.29%).

TABLE 18. TOTAL ORGANICS CONTENT

	Flow	Composite			Light Ends			Total
Sample	M^3	ug*	ug/m^3		ug	ug/m^3		ug/m^3
1A #1	24.5	644.0	26.3**	(96.3)	23.4	1.0	(3.7)	27.3
1A #2	21.0	758.5	36.1	(98.4)	14.3	0.7	(1.6)	36.8
2A #1	22.7	824.4	36.3	(93.3)	58.4	2.6	(6.7)	38.9
2A #2	13.2	885.9	67.1	(95.2)	45.3	3.4	(4.8)	70.5
3A #1	34.4	1535.8	44.6	(99.8)	4.1	0.1	(0.2)	44.7
3A #2	26.1	515.2	19.7	(98.5)	6.4	0.2	(1.5)	20.0
4A #1	28.1	1359.4	48.4	(99.6)	5.3	0.2	(0.4)	48.6
4A #2	23.5	784.5	33.4	(94.9)	41.7	1.8	(5.1)	35.2
4A #3	21.9	675.4	30.8	(92.2)	57.0	2.6	(7.8)	33.4
1B	29.3	741.8	25.3	(98.3)	13.6	0.5	(1.9)	25.8
2B	47.5	993.3	20.9	(93.3)	70.1	1.5	(6.7)	22.4
3B	52.0	745.0	14.3	(99.3)	6.9	0.1	(0.7)	14.4
4B	42.7	1870.3	43.8	(95.7)	128.2	3.0	(4.3)	46.8

*in terms of BAP sensitivity

**Numbers in parentheses are % of total of all peaks Example 43.8 (95.7%)

High Performance Liquid Chromatographic Analysis

Samples were collected at four engine power settings using both a high sulfur and a low sulfur fuel. Duplicate samples were taken using the low sulfur fuel. These 12 samples were collected and extracted as described earlier.

Analysis was carried out using a DuPont Model 830 high performance liquid chromatograph with a DuPont Model 835 multiwavelength photometer having ultraviolet absorption and fluorescence detectors. The column was a 4.6mm ID x 25cm stainless steel column packed with Zorbax (microparticular silica support) octadecylsilane and was maintained at 50°C. The primary mobile phase was 75% methanol, 25% water and the secondary mobile phase was 100% methanol. A nonlinear gradient mode was used which averaged about 4% per minute. The mobile phase flow was 2.5 ml/min and the pressure was 2500 psig. The sample injected (by means of a valve) was 10ul.(32,22,34)

Calibration of the instrument was carried out using various 3, 4, 5 and 6 fused ring compounds. Table 19 gives the retention times and sensitivities for these substances.

TABLE 19. RETENTION TIMES AND AND SENSITIVITIES FOR HPLC KNOWNS

Compound	Retention Time min.	Response in Peak Height per ng Ultraviolet	Fluorescence	Number Fused Rings	Molecular Weight
Fluorene*	6.5	6×10^{-2}	-	3	166
Phenanthrene*	7.69	9.4×10^{-2}	3.58×10^{-1}	3	178
Anthracene*	7.72	4.93×10^{-1}	11.16	3	178
Benzacridine*	8.37	1.77	28.26	4	219
Fluoranthene*	8.90	1.46	88.45	4	202
Pyrene*	9.38	1.31×10^{-1}	1.41	4	202
Chrysene**	12.55	2.16×10^{-2}	1.02×10^{-1}	4	228
Benzo (a)anthracene*	14.9	1.2×10^{-1}	2.56	4	228
Benzo (e) pyrene*	17.35	5.36×10^{-2}	2.69×10^{-1}	5	252
Perylene**	17.9	1.18×10^{-1}	127.0	5	252
Benzo (a) pyrene*	20.3	1.11	28.44	5	252
Dibenz (ah) anthracene**	21.4	1.12×10^{-1}	2.25	5	278
Benzo (ghi) perylene**	22.9	8.96×10^{-1}	28.26	6	276
Phenylene pyrene**	23.1	1.15	144.2	6	276

* Samples used contained 1000 ng/ul
** Samples used contained 250 ng/ul

It is apparent from Table 19 that retention time, in general, increases with an increase in the number of fused rings and also with an increase in molecular weight e.g., compare chrysene with benzo (a) anthracene. Separation into individual compounds is not possible with the conditions used because of the closeness of the retention times. In addition many other compounds may be present. In this analysis effort was directed to determine the relative amounts of compounds containing a like number of fused rings or similar molecular weight. Tentative identifications, based on retention time data, are given for a few components in some samples. Absolute identifications of PAH compounds are given in the section on GC/MS. Table 19 also shows the differences in sensitivity from one compound to another and as a function of detector.

Tables 20 through 34 give the results for the samples analyzed. Some variation in retention times from the values for the knowns occurs due to instrument flow changes. Although the pressure on the instrument's mobile phase was easily set and controlled, the resulting flow showed some variation from day to day. Retention time calibrations were periodically repeated.

TABLE 20. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	 Fluorescence
1A No. 1	0.87		1862	-
	0.98			448
	1.08		144	6336
	1.18			T
	1.25		416	7040
	1.36		480	T
	1.47		272	-
	1.52			806
	1.57		346	-
	1.67			2112
	1.75		208	-
	1.91			1626
	2.00			T
	2.11			858
	2.18		206	-
	2.45		T	576
	2.63		T	3034
	2.75		T	-
	2.83		26	-
	3.00		T	-
	3.05			T
	3.10		144	960
	3.32		64	397
	3.65			2432
	3.76	Naphthalene	48	-
	3.85		T	T
	4.05			T
	4.22		T	730
	4.85		T	-
	5.07		11	1360
	5.40		T	-
	5.52		T	64
	5.88		5.2	-
	6.00		-	1366
	6.4		6.6	9440
	6.55		2.4	T
	6.69		-	T
	7.6	Anthracene	-	90 (21.68 ng)
	7.88		4	-
	8.38	Benzacridine	T	T
	8.65		3.6	T
	8.84	Fluoranthene	30	4864 (12.82 ng)
	9.27	Pyrene	14	102 (10.28 ng)
	12.3		-	64
	12.65		-	112
	17.45	Perylene	-	131 (0.79 ng)
	18.1		-	128
	22.37		6	T
	22.8	Benz (ghi) perylene		61 (0.35 ng)
	23.08	o-phenylene pyrene		48 (0.24 ng)
	Total Flow	24.6 m^3		

T = Trace

TABLE 21. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	Response in Peak Height Fluorescence
1A No. 2	0.87		5011	-
	0.93		T	496
	1.06			T
	1.12		208	-
	1.2			5120
	1.26		368	-
	1.33		496	-
	1.37			3328
	1.44		736	-
	1.48			572
	1.53		576	-
	1.62			3072
	1.70		352	-
	1.86			3405
	2.08		352	973
	2.25			T
	2.38		42	1024
	2.54		256	2867
	2.74		T	-
	2.87		32	-
	2.98		T	3123
	3.16		25.6	T
	3.70		16	2432
	5.13			307
	5.42		T	-
	5.53			6067
	5.88		24	1510
	6.05			1152
	6.90	Anthracene		121 (30.84 ng)
	7.83		104	-
	8.00	Fluoranthene	71.6	18176 (52.71 ng)
	8.40	Pyrene	43.4	333 (33.55 ng)
	8.5		T	-
	8.63		T	-
	11.53		2.6	281.6
	12.58			89.6
	16.45	Perylene	T	208 (1.26 ng)
	17.1		T	205
	20.23			43.2
	20.65		7.8	-
	22.33	Benz (ghi) perylene		70.4 (0.41 ng)
	22.62	o-phenylene pyrene	4	64 (0.32 ng)
		Total Flow	21.0 m^3	

TABLE 22. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	Response in Peak Height Fluorescence
2A No. 1	0.76		52.4	-
	0.84		53.6	T
	1.17		28	-
	1.2		-	133
	1.39		12.2	-
	1.48		15.4	-
	1.58		T	48
	1.68		28	-
	1.87		T	T
	1.99		T	-
	2.09		T	-
	2.20		T	-
	2.40		-	19
	2.57		T	-
	3.3		T	128
	3.66	Naphthalene	6	-
	5.4		-	T
	7.9	Fluoranthene	-	109 (0.2 ng)
	8.35		4.6	-
	15.55		7	-
	17.2		T	-
	17.9		T	-
	19.25		T	-
		Total Flow	22.7 m^3	

T = Trace

TABLE 23. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	Response in Peak Height Fluorescence
2A No. 2	0.84		5024	-
	1.2		-	736
	1.31		583	1600
	1.45		512	-
	1.5		-	384
	1.55		608	-
	1.62		-	1710
	1.72		T	-
	1.89		112	1920
	2.39		-	2016
	2.63		T	-
	2.80		44	-
	3.08		96	5216
	3.27		144	-
	3.58		-	371
	3.74		100	-
	3.86	Naphthalene	16	-
	4.2		36	3264
	4.45		T	-
	4.85		6	-
	5.0		8	-
	5.35		8	-
	5.55		-	240
	5.67		T	-
	6.35		-	80
	6.50		3.2	-
	7.60	Anthracene	T	T
	8.83	Fluoranthene	10.8	2432 (4.4ng)
	9.45	Pyrene	3.2	25.6 (2.6 ng)
		Total Flow	13.2 m^3	

T = Trace

TABLE 24. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	Response in Peak Height Fluorescence
3A No. 1	0.77		36	-
	1.2		23	67
	1.33		29	-
	1.45		12	-
	1.55		12.4	-
	1.70		T	-
	2.4		-	T
	2.6		-	32
	3.6		-	93
	8.3		3.6	T
	8.7	Fluoranthene	-	88 (0.56 ng)
	17.55		5.6	-
	18.8		4	-
	19.25		T	-
	20.43		4.2	-
	21.45		2.8	-
	22.8	Benzo (ghi) perylene	-	T
	23.1	o-phenylene pyrene	-	T
		Total Flow	32.4 m^3	

T = Trace

TABLE 25. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	Response in Peak Height Fluorescence
3A No. 2	0.75		26	-
	0.80		32	-
	1.17		T	90
	1.27		11.2	-
	1.38		T	-
	1.48		T	-
	3.32		-	64
	3.75	Naphthalene	4.4	-
	4.75		2.4	-
	7.5		-	T
	8.05	Fluoranthene	-	176 (0.32 ng)
	8.54		5.8	20.8
	16.5	Perylene	-	16 (0.1 ng)
	22.4	Benzo (ghi) perylene	-	25.6 (0.15 ng)
	22.85	o-phenylene pyrene	-	24 (0.12 ng)
		Total Flow	26.1 m^3	

T = Trace

TABLE 26. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	 Fluorescence
4A No. 1	0.75		20	-
	0.8		-	26
	0.88		44.8	-
	1.25		T	T
	1.33		8	-
	1.45, 1.55		T	T
	3.6		-	64
	8.37		3.2	-
	8.82	Fluoranthene	-	144 (0.26 ng)
	17.4	Perylene	-	T
	18.1		-	T
		Total Flow	26.4 m^3	

T = Trace

TABLE 27. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	 Fluorescence
4A No. 2	0.75		1320	-
	1.08		3112	-
	1.27		-	9600
	1.35		288	-
	1.65		-	678
	1.75		120	-
	2.15		32	-
	2.30		-	15.5
	2.55		-	38.4
	2.60		4	-
	2.95		33	1312
	3.12		T	-
	3.41		-	122
	3.54		18	-
	3.70		T	-
	3.87	Naphthalene	14.2	-
	3.93		-	1152
	4.52		4	-
	5.13		-	64
	8.08	Fluoranthene	-	224 (0.4 ng)
	8.50	Pyrene	1.4 (1 ng)	T
		Total Flow	18.1 m^3	

T = Trace

TABLE 28. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height	
			Ultraviolet	Fluorescence
4A No. 3	0.96		496	-
	1.03		-	213
	1.08		280	-
	1.13		T	T
	1.38		280	-
	1.41		-	5184
	1.55		T	-
	1.70		-	998
	1.75		88	-
	2.25		28	-
	2.30		-	112
	2.35		40	-
	2.62		11.2	58
	2.89		8.4	-
	3.05		T	906
	3.15		44	-
	3.27		T	T
	3.60		T	54
	3.70		136	-
	3.85	Naphthalene	6	-
	3.98		21.2	-
	4.08		-	T
	4.2		-	406
	4.6		-	58
	4.83		7.6	-
	8.8	Fluoranthene	T	227 (0.41 ng)
	9.37		13	-
	16.70		12	-
		Total Flow	23.5 m^3	

T = Trace

TABLE 29. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height	
			Ultraviolet	Fluorescence
1B	0.72		464	-
	0.9		-	1290
	1.05		T	2752
	1.19		56	1664
	1.27		-	4224
	1.33		304	-
	1.48		92	1242
	1.54		52	-
	1.62		116	3904
	1.9		-	1126
	1.96		T	-
	2.08		-	640
	2.14		528	-
	2.37		T	5632
	2.58		12	1024
	2.80		12	-
	3.04		10	307
	3.3		T	1075
	3.6		-	3840
	3.67		T	-
	4.05		-	T
	4.15		T	T
	4.58		-	80
	4.75		2.6	-
	5.0		13.4	16.64
	5.42		3	58
	5.78		4	96
	6.35		6	1312
	6.65		5	-
	6.9		-	70
	7.53	Anthracene	-	144 (34.7 ng)
	7.80		T	-
	7.92		-	T
	8.23	Benzacridine	-	48 (0.31 ng)
	8.40		T	-
	8.55		-	134
	8.75	Fluoranthene	18.4 (7.86 ng)	4128 (7.42 ng)
	9.25	Pyrene	2.4	64 (6.5 ng)
	9.85		-	96
	12.5		-	96
	13.6		-	96
	15.55		-	48
	17.4	Perylene	T	288 (1.74 ng)
	18.0		-	136
	20.65		-	40
	21.1		-	40
	22.3		-	32
	22.8	Benzo (ghi) perylene	-	80 (0.46 ng)
	23.1	o-phenylene pyrene	-	64 (0.32 ng)
	24.75		-	176
		Total Flow	29.3 m^3	

T = Trace

TABLE 30. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	Response in Peak Height Fluorescence
2B	0.76		56	-
	0.80		-	256
	0.97		-	968
	1.10		6	-
	1.20		T	-
	1.30		3	-
	1.44		T	-
	1.48		-	T
	1.53		2	-
	1.63		-	42
	1.75		8.6	-
	2.49		-	45
	2.60		2.8	-
	3.05		-	62
	3.32		-	78
	4.12		-	54
	4.41		-	T
	4.62		-	123
	5.52		-	46
	6.45		-	32
	6.75		5	-
	8.8	Fluoranthene	-	176 (0.3 ng)
	9.3	Pyrene	T	19.2 (1.94 ng)
		Total Flow	47.m^3	

T = Trace

TABLE 31. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	Response in Peak Height Fluorescence
2B	0.75		64.8	-
	0.8		-	141
	1.0		-	1024
	1.21		4.2	1446
	1.33, 1.45, 1.54		T,T,T	-
	1.64		-	64
	1.75		14	-
	2.0		-	T
	2.63		8	-
	3.08		3.2	109
	3.82		-	115
	4.1		-	64
	4.67		-	186
	5.58		-	77
	6.55		-	77
	8.91	Fluoranthene	T	346 (0.62 ng)
		Total Flow	47.5 m^3	

T = Trace

TABLE 32. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height	
			Ultraviolet	Fluorescence
3B	0.75		68	256
	0.85		-	3
	1.04		-	2195
	1.22		-	2790
	1.30		10	-
	1.43, 1.52		T,T	-
	1.6		T	128
	1.72		T	-
	2.2		-	109
	3.1		4.8	128
	3.58		-	128
	4.15		-	64
	4.58		-	218
	6.55	Hexane disturbance	-	77
	8.8	Fluoranthene	T	314 (0.57 ng)
		Total Flow	42.4 m^3	

T = Trace

TABLE 33. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height	
			Ultraviolet	Fluorescence
3B	0.78		88	-
	0.88		-	256
	0.97		4	3072
	1.0		T	T
	1.5		-	3168
	1.20		6	-
	1.31		8	-
	1.43		4	-
	1.52		2.4	T
	1.60		-	186
	1.70		9.6	-
	1.89		T	T
	2.00		T	T
	2.28		T	-
	2.45		T	96
	3.05		4	96
	3.3		-	T
	3.65		-	80
	4.2		4	48
	4.62		-	144
	5.5		T	T
	8.82	Fluoranthene	-	112 (0.2 ng)
	14.00		3.6	-
		Total Flow	42.4 m^3	

T = Trace

TABLE 34. HPLC ANALYSIS

Sample	Retention Time, min	Identity	Response in Peak Height Ultraviolet	Response in Peak Height Fluorescence
4B	0.78		259	-
	0.97		-	461
	1.06		T	-
	1.15		24	-
	1.21		-	T
	1.30		37	2624
	1.55		-	128
	1.62		T	-
	1.67		10	-
	2.13		T	-
	2.33		T	T
	2.78		5.2	294
	2.95		-	T
	3.23		T	32
	3.75		T	192
	4.45		4	-
	4.73		8	-
	4.85		-	64
	5.73		-	80
	7.5	Benzacridine	-	76.8 (0.49 ng)
	7.82	Fluoranthene	-	304 (0.55 ng)
	8.23	Pyrene	4	64 (6.45 ng)
	8.43		9.2	-
		Total Flow	42.7 m^3	

T = Trace

In order to put this data in perspective, it is necessary to correct for differences in total flow and to attempt to relate the number of fused rings to relative abundances. In Table 35, the responses were totaled for UV detector responses and also for fluorescence detector responses for components having retention times up to 6 minutes, between 6 and 15 minutes and over 16 minutes. Generally, compounds having 3 or 4 fused rings elute between 6 and 16 minutes; compounds having 5 or 6 fused rings elute in 16+ minutes. Compounds with fewer than 3 fused rings elute in less than 6 minutes (see Table 19). This is only a very rough approximation because as shown in Table 19, the sensitivity in terms of response per nanogram ranges from 0.006 to 1.7 for 3 or 4 fused ring compounds with the ultraviolet absorption detector, and from 0.36 to 88 in the case of the fluorescence detector. With 5 or 6 fused rings, the ranges are 0.05 to 1.15 with the UV absorption detector and 0.27 to 144 with the fluorescence detector.

TABLE 35. HPLC - TOTAL ULTRAVIOLET ABSORPTION AND FLUORESCENCE RESPONSES

	Responses, Total Peak Height												
	Under 3 rings				3 - 4 rings				5 - 6 rings				
Sample	UV		Fl		UV		FL		UV		Fl		Total Flow
1B	1669	(98%)	28961	(80.3%)	31	(2%)	6236	(17.3%)	T		856	(2.4%)	29.3
2B	78	(94%)	1674	(88.1%)	5	(6%)	227	(11.9%)	-			-	47.5
2B	94	(100%)	3226	(88.4%)	-	-	423	(11.6%)	-	-	-	-	47.5
3B	130	(97%)	7146	(98.4%)	4	(3%)	112	(1.6%)	-	-	-	-	42.4
3B	83	(100%)	6019	(95 %)	-	-	314	(5 %)	-	-	-	-	42.4
4B	347	(96.4%)	3875	(89.7%)	13	(2.6%)	445	(10.3%)	-	-	-	-	42.7
1A #1	3545	(98.1%)	28779	(63.7%)	61	(1.7%)	16038	(35.5%)	6	(0.2%)	368	(0.8%)	24.6
1A #2	8254	(98.3%)	60046	(75.4%)	128	(1.5%)	19008	(23.9%)	12	(0.2%)	591	(0.7%)	21.0
2A #1	196	(94.2%)	328	(76.8%)	12	(5.8%)	109	(23.2%)	-	-	-	-	22.7
2A #2	7167	(99.7%)	17457	(87.6%)	18	(0.3%)	2458	(12.4%)	-	-	-	-	13.2
3A #1	112	(87.1%)	192	(68.6%)	3.6	(2.8%)	88	(13.4%)	13	(10.1%)	T	-	32.4
3A #2	76	(100%)	154	(38.9%)	-	-	176	(44.4%)	-	-	66	(16.7%)	26.1
4A #1	73	(95.8%)	90	(38.5%)	3.2	(4.2%)	144	(61.5%)	-	-	T	-	26.4
4A #2	4945	(100%)	13120	(98.4%)	-	-	224	(1.6%)	-	-	T	-	18.1
4A #2	1446	(98.3%)	7989	(97.2%)	13	(0.9%)	227	-	12	(0.8%)	-	-	23.5

In Table 35, one may note that the percent of the total response of the sample is very high for compounds with less than 3 fused rings, with the ultraviolet absorption detector, generally well above 90%. The less than 3 fused ring category also commands a major portion of the fluorescence response. Thus most of the materials collected were in this category. The number in parentheses in the table is the percent of the total.

Table 36 shows the relative reponse per cubic meter of flow. The high sulfur samples show a large decrease in total response in all categories from idle to higher powers. No large fused ring compounds were found except at idle. The low sulfur samples show a similar decrease with again virtually no 5-6 fused ring compounds except at idle. The sample, asterisked on Table 36, with very low total flow, seems to give unusually high values for responses. Due to water in the Magnahelic gauges flow measurements are subject to inaccuracies in any case. Values for low sulfur fuel runs are in general higher than for high sulfur fuel runs. One other very important variable is the effect of temperature and flow on recovery of PAH such as benzo (a) pyrene (already discussed), which is a 5 fused ring compound. Even poorer recovery would be expected with smaller, more volatile substances.

These results correspond well with those for the polynuclear aromatic hydrocarbons measured by GC/MS which reported higher PAH values for low sulfur fuels than for high sulfur fuels and a lowering of PAH with increase in power. Differences noted in the GC/MS work between samples labeled nA No. 1 and nA No. 2 again appear but concur also with lower total flows for nA No. 2 versus nA No. 1.

TABLE 36. HPLC-TOTAL-RESPONSE/m^3 FLOW

Sample	Under 3 rings		3 - 4 rings		5 - 6 rings	
	UV	FL	UV	FL	UV	FL
1B	57.0	988.4	1.1	212.8	-	29.2
2B	1.6	35.2	0.1	4.8	-	-
2B	2.0	67.9	-	8.9	-	-
3B	3.1	168.5	0.1	2.6	-	-
3B	2.0	142.0	-	7.4	-	-
4B	8.1	90.7	0.3	10.4	-	-
1A #1	144.1	1169.9	2.5	652.0	0.2	15.0
1A #2	393.0	2859.3	6.1	905.1	0.6	28.1
2A #1	8.6	14.4	0.5	4.8	-	-
2A #2	543.0	1322.5	1.4	186.2	-	-
3A #1	3.4	5.9	0.1	2.7	0.4	T
3A #2	2.9	5.9	-	6.7	-	2.5
4A #1	2.8	3.4	0.1	5.4	-	T
4A #2*	273.2	724.9	-	12.4	-	T
4A #2	61.3	340.0	0.6	9.6	0.5	-

*Very low total flow

GAS CHROMATOGRAPH-MASS SPECTROMETER ANALYSES

Sixteen filters from the four power points with both high sulfur and low sulfur fuels were extracted with hexane as described previously. In addition to these sixteen filters, representing duplicates for each power point for each fuel, a third filter was processed for one of the points, namely takeoff with low sulfur fuel.

The extracts were concentrated by controlled, low temperature evaporation to a volume of one milliliter each and delivered to Arthur D. Little, Inc. for their analysis on a Finnegan Model 4000 mass spectrometer coupled with a Finnegan gas chromatograph. The chromatographic column was a 20 meter glass capillary column coated with OV-101 (methyl silicone).

One microliter samples were injected using a Grobe type splitless injection. The temperature program for the column oven was 55°C for 1.1 min. followed by a linear gradient of 25.5°C/min. to a temperature of 150°C, and a second linear gradient of 4°C/min to a temperature of 260°C. Finally, the 260°C temperature was maintained for 10 minutes. Mass spectrometric conditions are given in Table 37.

TABLE 37. MASS SPECTROMETRIC CONDITIONS

Finnigan Model 4000 mass spectrometer

(a)	Mass range	100 - 310 amu
(b)	Integration	10 ms/amu
(c)	Electron multiplier	1800V
(d)	Electron energy	70eV
(e)	Filament emission	30 ma
(f)	Scan rate	1 sec/spectrum

For the quantitative set of GC/MS analysis, the samples requiring concentration were evaporated under dry nitrogen from 1 ml to 100μl for a tenfold effect. The other samples were simply kept as 1 ml volumes. (See Table 38 for the division of the samples). In both cases, phenylanthracene was added as an internal standard to give a concentration of 0.5 ng/μl in the final analyzed sample volume. For the concentrated samples, the appropriate amount of phenylanthracene was added midway through the evaporation step.

Addition of internal standard to each of the samples allows correction of the daily instrument variations, giving an accurate comparison of the PAH levels among the samples, provided calibration data are available. The quantity of internal standard added to the sample should be in large excess of the quantity of that material originally present, while not being sufficiently large to degrade GC column performance. The initial survey of the samples indicated that the maximum signal for phenylantracene in the samples, found in 1A#2, was less than 100 units. A 0.5 ng sample of phenylanthracene gives a signal of more thand 5000 units for the conditions listed in Tables 38 and 39. Thus, the maximum error to the signal of the internal standard is less than 2% due to residual phenylanthracene.

To determine calibration factors for specific PAH compounds, a commercially available mixture of 10 PAH compounds, Supelco Catalog #4-9155, was diluted to 1 ng/ul of each PAH compound. The individual components of the commercial mixture are listed in Table 40. Phenylanthracene (0.5 ng/ul) was added to make up the final calibration mixture. Replicate analyses of the calibration mixture give calibration or response factors to adjust for the observed dependence of instrumental sensitivity to the different PAH compounds. Table 41 lists the calibration factors for each component of the standard PAH mixture obtained from the areas of the mass chromatographic peaks of the appropriate molecular ion. This mixture covers the molecular weight span of the observed sample species, but not all of the individual PAH compounds.

TABLE 38. TEST AND EXPERIMENTAL PARAMETERS FOR EACH SAMPLE

Sample Designation	Power Setting	Sulfur Content	Analysis Concentration
1A#1	1 (low)	low	none
1A#2	1	low	none
1B#1	1	high	none
1B#2	1	high	none
2A#1	2	low	10X
2A#2	2	low	none
2B#1	2	high	10X
2B#2	2	high	none
3A#1	3	low	10X
3A#2	3	low	10X
3B#1	3	high	10X
3B#2	3	high	10X
4A#1	4 (high)	low	none
4A#2	4	low	none
4A2 rep.	4	low	none
4B#1	4	high	10X
4B#2	4	high	10X

TABLE 39. GAS CHROMATOGRAPHIC CONDITIONS

a) 20 meter glass capillary column coated with OV-101

b) Grobe type - splitless injection

c) Multilinear temperature program

   1) 55° isothermal program for 1.1 min
   2) 55°C - 150°C linear program at 25.5°C min
   3) 150°C - 260°C linear program at 4°C/min
   4) 260°C isothermal program for 10 min

d) 1 ul sample injections

TABLE 40. PAH STANDARD COMPOSITION

1 ng/μl

Phenanthrene
Anthracene
Pyrene
Fluoranthene
Triphenylene
Benz(a)anthracene
Chrysene
Perylene
Benzo(a)pyrene
Benzo(e)pyrene

TABLE 41. CALIBRATION FACTORS FOR THE STANDARD PAH MIXTURE

Compound	Calibration Factor	Average Factor for Cluster
Phenanthrene	2.19	2.90
Anthracene	3.61	
Pyrene	2.42	2.54
Fluoranthene	2.66	
Triphenylene	1.23*	1.23
Bednz(a)anthracene	1.23*	
Chrysene	1.23*	
Benzo(e)pyrene	.734	.701
Benzo(a)pyrene	.565	
Perylene	.804	
Phenylanthracene	1.00**	

*peaks not separable
**by definition (internal standard)

For those PAH compounds for which calibrating materials were not available, response factors were computed from a least squares fit, as a function of molecular weight, of the response factors for the standard materials. These response factors were then used to correct the GC peak areas specific to the individual PAH species to give the reported quantitative data.

To identify non-PAH organic species, a wider mass range analysis was run on the sample with the highest PAH concentration, 1A#2. The species identified from this GC/MS run were then measured in the remaining samples, relative to the phenylanthracene internal standard for each run. All species, PAH and other, were identified by comparison with reference MS spectra and correlated with relative GC retention times.

In the analyses of the seventeen samples, specific identifications were made of PAH and of oxygenate derivatives. Figure 29 shows a representative mass spectrogram of a sample (1A #2) with specific identifications. PAH with 3 and 4 fused rings such as fluorene, fluoranthene, anthracene and pyrene are much more abundant and represent the main components in the samples (35,36). PAH with 5 and 6 fused rings such as perylene, and benzopyrenes are much less abundant and indeed at power settings above idle are generally not detectable. The amount of oxygenated compounds and nitrogen or sulfur containing species are greater in magnitude than found for PAH at the same power settings and same fuel. This observation is especially apparent at higher engine settings.

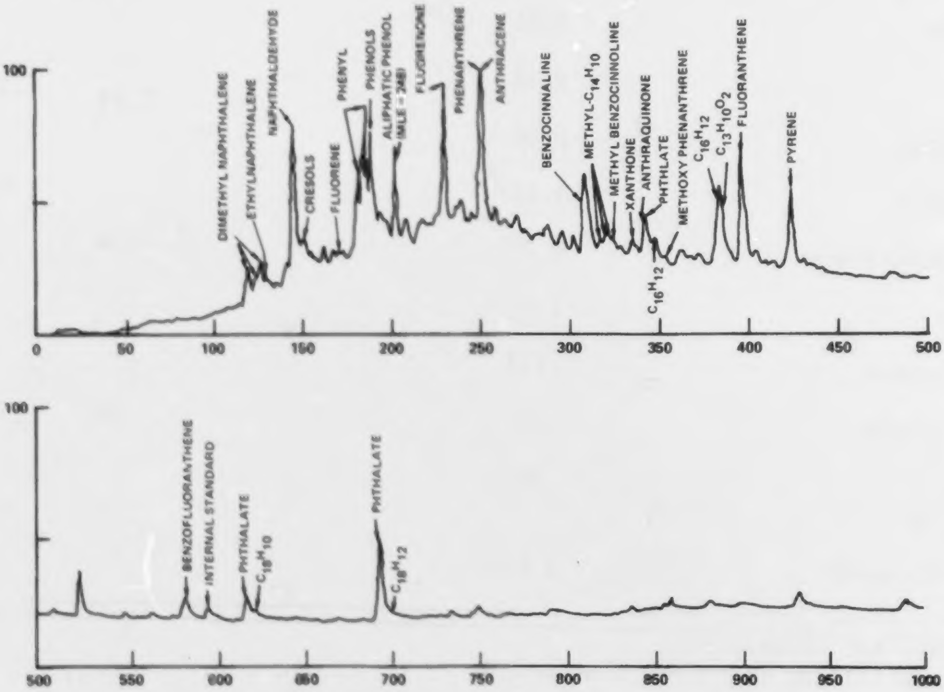


Figure 29. Representative mass spectrogram.

The quantitative aspects of the results serve to give indications of trends only. Absolute magnitudes are subject to several variables which markedly affect them. These variables include uncertainties in flow measurement, and stability of species as a function of temperatures and flow.

Tables 42, 43, 44, and 45 give the amounts found in nanograms/m^3 for the data. Corrections for flow differences between the samples have been made. The concentration of PAH materials found in each sample shows consistent patterns throughout the samples. The trends described previously show the behavior of PAH concentrations as a function of test parameters. More specifically, the distribution of PAH materials seems to be a function of the power setting. If one considers the four sets of compounds for which there is direct calibration, anthracene/phenanthrene (m/e 178), fluoranthene/ pyrene (m/e 202), benzophenanthrene/chrysene/naphthacene (m/e 228), and benzo(a) pyrene/benzo(e)pyrene/perylene (m/e 252), the level of PAH material maximizes at the m/e 202 (fluoroanthene/pyrene) cluster for samples taken at low power while it maximizes at m/e 178 (anthracene/phenanthrene) for the remaining samples. That is to say that the lower power settings not only generate relatively higher PAH levels but relatively higher molecular weights as well. The high mass species, m/e 228 and 252, are rapidly attenuated as the power setting increases.

TABLE 42. GC/MS ANALYSIS-PAH (NG/M^3)

Carcinogenicity		Species	m/e	1A #1	1A #2	2A #1	2A #2	3A #1	3A #2	4A #1	4A #2	4A #3
-	fluorene	$C_{13}H_{10}$	166	3.85	7.52	1.89	13.86	0.18	0.33	0.09	8.65	1.60
-	anthracene-	$C_{14}H_{10}$	178	106.0	223.8	3.43	659.7	1.14	0.14	0.53	68.30	56.62
-	phenanthrene											
	methyl fluorene	$C_{14}H_{12}$	180	2.57	ND	0.06	11.63	0.09	0.03	0.78	10.17	6.21
	methyl-C14H10	$C_{14}H_{12}$	192	27.85	76.19	0.06	136.4	ND	ND	0.50	1400	72.60
-	fluoranthene	$C_{16}H_{10}$	202	133.6	232.3	1.20	278.3	0.18	0.47	ND	2.61	18.60
-	pyrene	$C_{16}H_{10}$	202	46.79	1195.2	0.69	90.70	0.12	0.11	ND	1.78	16.62
-	aceanthralyene	$C_{16}H_{12}$	204	13.96	29.10	ND	79.84	ND	ND	ND	ND	ND
-	benzofluorene	$C_{17}H_{12}$	216	16.19	30.62	ND	7.13	ND	ND	ND	ND	ND
- to ++	benzofluoranthene	$C_{18}H_{10}$	226	67.17	94.76	ND	13.88	ND	ND	ND	ND	ND
+++	benzophenanthrene											
±	chrysene,											
-	naphthacene	$C_{18}H_{12}$	228	48.68	86.66	ND	6.98	ND	ND	ND	ND	ND
+++	benzopyrenes	$C_{20}H_{12}$*	252	37.62	43.19	ND	ND	ND	ND	ND	ND	ND
-	perylene	$C_{20}H_{12}$	252	12.11	19.67	ND	ND	ND	ND	ND	ND	ND
	Totals			517.0	2038.1	5.7	1302.3	1.8	1.1	1.9	108.7	173.5
		Flow,m^3		26.5	21	17.5	12.9	32.4	36.1	32	23	21.9

* = Sum of signals for both benzo (a) and benzo (e) pyrene, with benzo (e) pyrene contributing much more to the signal than benzo (a) pyrene.

ND = below instrumental detection limit of 0.010 ug/ml, or 0.001 ug/ml for 10X concentrated samples. (Total Sample)

- = non-carcinogenic

± = uncertain

+ = carcinogenic

+++, etc. = strongly carcinogenic

TABLE 43. GC/MS ANALYSIS-PAH

Species		m/e	1B #1	1B #2	2B #1	2B #2	3B #1	3B #2	4B #1	4B #2
fluorene	$C_{13}H_{10}$	166	0.58	5.04	0.25	0.27	2.66	0.13	0.32	0.10
anthracene-phenanthrene	$C_{14}H_{10}$	178	22.12	34.06	3.34	26.95	9.25	1.33	3.57	0.61
methyl fluorene	$C_{14}H_{12}$	180	ND	1.21	0.02	0.57	5.71	0.07	0.42	ND
methyl-C14H10	$C_{15}H_{12}$	192	5.56	9.65	0.59	4.06	42.5	0.45	4.55	0.50
fluoranthene	$C_{16}H_{10}$	202	36.86	42.58	0.42	34.10	0.77	0.36	0.79	0.61
pyrene	$C_{16}H_{10}$	202	3.99	9.69	0.23	1.87	ND	0.31	0.42	0.40
aceanthralyene	$C_{16}H_{12}$	204	2.29	3.44	ND	0.23	ND	ND	ND	ND
benzofluorene	$C_{17}H_{12}$	216	3.31	6.99	ND	0.80	ND	0.18	ND	ND
benzofluoranthene	$C_{18}H_{10}$	226	33.17	42.19	ND	1.37	ND	ND	ND	ND
benzophenanthrene chrysene, naphthacene	$C_{18}H_{12}$	228	24.10	25.70	ND	0.34	ND	0.02	ND	ND
benzopyrenes	$C_{20}H_{12}$*	252	41.30	22.66	ND	ND	ND	ND	ND	ND
perylene	$C_{20}H_{12}$	252	5.53	7.93	ND	ND	ND	ND	ND	ND
dibenzothiophene	$C_{12}H_8S$	184	2.83	5.58	0.06	1.66	ND	ND	1.82	0.61
Totals			180.9	214.8	4.2	71.6	23.6	2.2	10.6	2.1
	Flow, m^3	2.3	29.3	25.6	47.6	47.5	50.8	44.8	37.8	47.6

* Sum of signals for both benzo (a) and benzo (e) pyrene, with benzo (e) pyrene contributing much more to the signal than benzo (a) pyrene.

ND = below instrumental detection limit of 0.010 ug/ml, or 0.001 ug/ml for 10X concentrated samples. (Total Samples)

TABLE 44. GC/MS ANALYSIS-OTHER COMPOUNDS

Species		m/e	1A #1	1A #2	2A #1	2A #2	3A #1	3A #2	4A #1	4A #2	4A #3
dimethyl & ethyl napnthalenes	$C_{12}H_{12}$	156	98.49	107.6	32.11	53.49	5.25	9.86	6.06	202.2	20.63
napnthaldehyde	$C_{11}H_8O$	156	452.8	804.8	10.23	1170.5	0.49	ND	0.59	686.9	110.0
phenyl phenols	$C_{12}H_{10}O$	170	535.8	1346.2	5.60	2279.1	ND	ND	ND	756.5	66.21
fluorenone	$C_{13}H_8O$	180	296.6	647.6	76.00	1426.4	16.33	29.08	16.25	181.7	80.36
benzocinnolines	$C_{12}H_8N_2$	180	180.8	371.4	145.1	528.7	41.36	39.06	ND	7.78	ND
methyl-benzo-cinnolines	$C_{13}H_{10}N_2$	194	106.8	193.3	17.77	554.4	ND	ND	ND	71.30	40.00
xanthones	$C_{13}H_8O_2$	196	49.81	122.9	2.06	362.0	1.73	ND	1.75	10.17	2.65
hydroxy-benzophenone	$C_{13}H_{10}O_2$	198	312.5	504.8	2.80	1682.2	ND	ND	ND	2.96	16.80
anthraquinone	$C_{14}H_8O_2$	208	58.49	100.9	2.91	293.0	ND	ND	ND	ND	10.55
methoxy-phenanthrene	$C_{15}H_{12}O_2$	208	20.94	5.19	2.97	27.05	ND	ND	ND	ND	5.25
-cresols	$C_{15}H_{24}O$	220	6.87	11.0	16.29	22.40	21.85	44.32	92.50	41.43	155.25
-phenols	$C_{17}H_{28}O$	248	39.25	71.43	49.14	50.70	18.81	25.76	35.00	72.17	19.5
Totals			2158.5	4314.3	365.17	8449.6	108.0	146.8	153.1	2447.8	529.7
	Flow, m^3		26.5	21	17.5	12.9	32.4	36.1	21	23	21.9

ND = below instrumental detection limit of 0.010 ug/ml, or 0.001 ug/ml for 10X concentrated samples. (Total Sample)

TABLE 45. GC/MS ANALYSIS-OTHER COMPOUNDS

Species		m/e	1B #1	1B #2	2B #1	2B #2	3B #1	3B #2	4B #1	4B #2
dimethyl & ethyl naphthalenes	$C_{12}H_{12}$	156	12.70	205.5	4.37	3.96	20.08	1.14	1.64	1.41
napthaldehyde	$C_{11}H_8O$	156	93.86	433.6	2.82	31.37	45.08	2.23	9.52	3.15
phenyl phenols	$C_{12}H_{10}O$	170	79.86	218.8	1.76	29.47	47.24	1.92	13.68	2.58
fluornone	$C_{13}H_8O$	180	95.22	80.08	2.50	137.5	23.23	1.94	5.05	1.76
benzocinnolines	$C_{12}H_8N_2$	180	321.8	140.6	ND	5.22	ND	11.80	ND	0.13
methyl-benzo-cinnolines	$C_{13}H_{10}N_2$	194	35.15	27.62	1.11	50.74	ND	1.32	4.10	1.39
xanothones	$C_{13}H_8O_2$	196	42.32	24.22	0.55	86.53	ND	1.36	0.74	0.50
hydroxy-benzophenone	$C_{13}H_{10}O_2$	198	604.1	161.3	1.95	652.6	ND	2.25	2.38	1.83
anthraquinone	$C_{14}H_8O_2$	208	40.61	27.15	0.06	(95.16)*	1.38	(0.36)*	0.92	ND
methoxy-phenanthrene	$C_{15}H_{12}O$	208	6.38	ND	0.19		ND		1.38	ND
-cresols	$C_{15}H_{24}O$	220	5.70	9.96	0.84	4.74	25.59	2.03	4.81	1.60
-phenols	$C_{17}H_{28}O$	248	4.20	95.31	0.61	7.85	25.00	5.94	3.25	2.58
Totals			1341.3	1421.9	16.8	1105.3	187.0	31.2	47.6	16.8
	Flow, m^3	2.3	29.3	25.6	47.6	47.5	50.8	44.8	37.8	47.6

*Chromatographic overlap of the two components prevented individual readings from being taken.

ND = below instrumental detection limit of 0.010 ug/ml, or 0.001 ug/ml for 10X concentrated samples. (Total Sample)

All of the samples from high sulfur fuel showed a decrease of the levels of PAH materials compared to the low sulfur set. This decrease was substantially greater than can be accounted for by the formation of dibenzthiophene at the observed level. The low abundance of sulfur species could be due to preferential formation of lower molecular weight material that would not have been trapped in the hot filter in the original collections.

The oxygenated species show a much less regular pattern than is seen in the PAH data. The power level does not show the marked effect that is observed for the PAH species, and scatter is apparent at the individual species level. However, when the total heteroelement material is compared, other trends very similar to those of the PAH compounds are observable. Samples from low sulfur fuel show more total heteroelement material than do the high sulfur samples, generally. Similarly, with the exception of two species, anthraquinone and hydroxybenzophenone, thé totals for each of the species for all of the low sulfur samples is greater than for all of the high sulfur samples.

The general results are as follows:

1) Low power settings yielded higher PAH levels and more PAH species than did the higher power settings.

2) Low sulfur fuels gave generally higher PAH and aromatic oxygenate levels than did high sulfur fuels.

3) PAH species distribution maximizes at the m/e (mass to charge ratio) of 202, $C_{16}H_{10}$ cluster (fluoranthene and pyrene) for the lowest power setting, and at the m/e of 178, $C_{14}H_{10}$ cluster (anthracene and phenanthrene) for the higher power settings.

4) PAH species m/e of 204 and higher fell below the detection limit at the higher power settings.

5) Replicate samples (same power setting and fuel) showed variations in magnitudes of species found. Variation between replicate samples seem to again follow the effect of total flow. The lower the total flow generally the higher the amounts found per m^3. The correlation applies also to the high sulfur fuels for the most part and to all tables.

6) Dibenzothiophene was detected in the high sulfur samples but was not detected in the low sulfur samples.

The total organics measurement gives an indication of the total organic matter adsorbed on the particulates. The HPLC measurement indicates the general magnitude of the 3-6 fused ring compounds. Tables 42 and 43 indicate the specific 3-6 fused ring compounds and their magnitudes. Tables 44 and 45 indicate other specific compounds formed including two fused ring compounds and oxygenated derivatives.

Packed Bed Filter Studies

This contract mandates the collection and analysis of the particulate matter emitted by a gas turbine engine. This interest was based on health considerations associated with particulate matter. A question remains as to whether the major part of the organic matter is adsorbed on these particulates or is emitted into the air as a vapor or aerosol and not collected on the filter. To gain some information on this matter, a series of experiments was carried out using a packed bed filter to collect both the particulate matter and these other organic species not adsorbed on the particulate matter.

Packed bed filters were 1/2" O.D. x 6" to 8" long stainless steel tubes packed with 7 to 12 grams of Chromosorb 102 (styrenedivinylbenzene polymeric material). The Chromosorb 102 material was prewashed with ethyl alcohol, methylene chloride and finally n-pentane, as described by Arthur D. Little, Inc. (29) to remove any soluble organic material before the Chromosorb 102 was placed in the tubes. Samples of engine exhaust gases were passed through the packed bed from the engine operating at approach and climb power settings using low sulfur fuel, and idle and climb power settings using high sulfur fuel. The volume of gas sampled was between 0.3 and $0.7 m^3$.

After collection of the organic material on the packed beds, the packing material was removed and extracted with hexane as described previously. This extract was analyzed for (1) total organics, (2) PAH by GC/MS and (3) boiling point distribution by methods and procedures also described elsewhere.

Table 16 gave the calibration data for various knowns in the total organics analyses. Recalibration of the instrument showed some change in sensitivity, e.g., fluorene 126.8 div/ng and the composite peak 23.55 div.^{2}/ng. Table 46 gives the results of the total organics analyses and Table 47 gives the total ng/m^3 for the samples. On comparison with the totals from the samples of extracts of particulates only, one finds the organic level to be much higher for the Chromosorb 102 samples at like power settings with the same fuel. Table 48 shows the differences. The organic material on the particulates represents 0.03 to 0.29% of the total collected on the packed bed filter.

TABLE 46. CHROMOSORB 102 SAMPLES - TOTAL ORGANIC ANALYSES

Sample	Retention Time Minutes	Response	
		Peak Height	Peak Area
2A	0.63	5760	-
	0.82	4640	-
	0.9	27200	-
	1.37	1840	-
	1.62	5920	-
	2.27	8480	-
	2.92	1600	-
	3.95	5840	-
	6.98*	77120	175833
3A	0.63	101760	-
	0.80	6080	-
	0.90	185600	-
	1.35	9600	-
	1.62	24960	-
	2.25	41920	-
	2.92	8320	-
	3.3	4800	-
	3.93	231200	-
	6.77*	207680	548275
1B	0.45	28480	-
	0.63	50880	-
	0.82	21760	-
	0.9	180800	-
	1.05	4800	-
	1.28	25920	-
	1.62	22720	-
	2.27	38720	-
	2.92	5120	-
	3.95	21120	-
	6.98*	138880	361088

*After flow reversed

(Continued)

TABLE 46. (Continued)

Sample	Retention Time Minutes	Response Peak Height	Response Peak Area
3B	0.63	12960	-
	0.82	2400	-
	0.9	27680	-
	1.03	37600	-
	1.38	2880	-
	1.62	2240	-
	1.83	5440	-
	2.12	18080	-
	2.27	4640	-
	2.92	12640	-
	4.0	6240	-
	7.13*	178560	326765

*After flow reversed

TABLE 47. CHROMOSORB 102 SAMPLES - TOTAL ORGANIC ANALYSES

Sample	Flow m^3	Composite ug	Composite ug/m^3	Light Ends ug	Light Ends ug/m^3	Total ug/m^3
2A	0.62	7466.4	12042.5	320.9	517.6	12560.1
3A	0.29	23281.3	80280.3	527.0	18172.4	98452.7
1B	0.36	15332.8	42591.1	1777.5	4937.5	47528.6
3B	0.71	13875.4	19542.8	715.4	1007.6	20550.4

TABLE 48. TOTAL ORGANICS ANALYSES COMPARISON

Sample	Source	Total ug/m^3
2A	Particulates	36.8 (0.29%)*
	Chromosorb 102	12560.1
3A	Particulates	average 32.35 (0.03%)
	Chromosorb 102	98452.7
1B	Particulates	25.8 (0.05%)
	Chromosorb 102	47528.6
3B	Particulates	14.4 (0.07%)
	Chromosorb 102	20550.4

*Using data for higher flow sample only

A. D. Little examined hexane extracts of these packed bed filters for PAH levels. The same chromatograph-mass spectrometer system was used by A. D. Little, Inc. as in the earlier work discussed in the section on GC-MS. The temperature program in the chromatograph was modified to accommodate the higher vapor pressure species trapped on the resin compared to the filter. The program was as follows:

1. 55°C injection with 0.8 min. hold
2. 55° to 75°C at 25.5°/min.
3. 75° to 160°C at 4°/min.
4. 160° to 260°C at 10°/min.
5. 260° isothermal for 10 min.

The results are given in Table 49 for the amounts found in terms of ng/m^3 of exhaust gas. Table 50 compares these totals for the specific PAH found on the Chromosorb 102 samples with those found on the particulates. The organic material on the particulates again represents only a very small fraction of the total, specifically 0.01 to 0.76%. Some indication exists in the very few samples used that the total organics decreases with power setting and with use of high sulfur fuel compared to low sulfur fuel.

The boiling point distribution analyses of the Chromosorb 102 samples (see Tables 51 through 58) showed no significant differences from those of the particulate extracts. The boiling point distribution is shown graphically in Figure 30 for only the sample collected at the idle power point using high sulfur fuel.

TABLE 49. PAH LEVELS FOUND IN CHROMOSORB 102 SAMPLES-GC/MS ANALYSIS

ng/m^3

Species	Composition	m/e	Sample 1B	 2A	 3A	 3B
Fluorene	$C_{13}H_{10}$	166	227.8	175.8	96.6	39.4
Anthracene/ Phenanthrene	$C_{14}H_{10}$	178	9527.8	118.7	3655.2	1260.6
Dibenzthiophene	$C_{12}H_8S$	184	130.6	12.9	ND	16.9
Methyl Anthr./Phen	$C_{15}H_{12}$	192	3444.4	295.2	1348.2	457.7
Fluoranthene	$C_{16}H_{10}$	202	2513.9	682.3	1041.4	398.6
Pyrene	$C_{16}H_{10}$	202	2363.9	614.5	1079.3	390.1
Aceanthrylene, etc.	$C_{16}H_{12}$	204	2972.2	230.6	1279.3	408.5
Benzofluorene	$C_{17}H_{12}$	216	766.7	67.7	300.0	115.5
Benzofluoranthene	$C_{18}H_{10}$	226	988.9	200.0	324.1	271.8
Benzanthracenes, Chrysene, etc.	$C_{18}H_{12}$	228	747.2	1661.3	420.7	171.8
Benzacridine	$C_{17}H_{11}N$	229	ND	203.2	ND	ND
Benzpyrenes	$C_{20}H_{12}$	252	1400.0	1308.1	303.4	278.9
Perylene	$C_{20}H_{12}$	252	916.7	408.1	648.3	133.8
Total			26000.1	7048.4	10496.5	3943.6

ND - Not detected. Instrumental Limit = 0.001 ug/ml

TABLE 50. TOTAL PAH LEVELS-GC/MS ANALYSIS

Chromosorb Samples vs. Filter Extracts

Sample	Packed Bed ng/m^3	Filters ng/m^3	% PAH Filters vs. Packed Bed
2A	7048.4	5.7*	0.08
3A	10496.5	1.5	0.01
1B	26000.1	197.8	0.76
3B	3943.6	12.9	0.33

*Using data only for higher flow sample

TABLE 51. BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - Chromosorb 2A (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
04 35	0.032	22 17	6.422
07 81	0.012	22 54	0.735
08 24	0.048	22 74	1.960
08 40	0.017	23 00	5.027
08 71	0.023	23 34	2.708
08 83	0.050	23 54	0.670
09 03	0.011	23 78	5.596
09 18	0.142	24 11	2.832
09 75	0.042	24 31	0.593
10 26	0.127	24 54	4.643
11 00	0.141	24 84	2.625
11 16	0.199	25 00	0.371
11 42	0.034	25 27	4.583
11 62	0.188	25 55	3.071
11 82	0.116	25 70	0.450
12 09	0.074	25 97	3.260
12 48	0.452	26 22	2.179
12 72	0.086	26 55	3.872
12 92	0.583	26 87	2.510
13 23	0.537	27 32	2.722
13 42	0.939	27 52	2.073
13 72	0.922	27 95	3.297
13 92	1.685	28 57	2.268
14 17	1.342	29 17	1.809
14 36	0.379	29 75	1.220
14 92	1.927	30 33	0.838
15 15	0.591	30 90	0.461
15 33	0.841	31 60	0.152
15 84	0.121	33 39	0.003
16 06	0.121	37 23	0.003
16 44	0.821		
16 98	1.768		
17 52	2.151		
18 04	0.931		
18 23	0.768		
18 53	2.039		
19 05	1.651		
19 48	1.281		
19 95	1.214		
20 15	0.449		
20 42	1.830		
20 56	1.908		
21 31	1.996		
21 71	1.600		
21 95	0.191		

TABLE 52. BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - Chromosorb 2A (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
03 34	0.078	16 71	1.048
04 09	0.060	16 92	2.986
05 97	0.003	17 27	1.403
06 76	0.116	17 69	2.872
06 95	0.135	17 90	2.623
07 16	0.097	18 11	2.988
07 46	0.292	18 52	3.462
07 61	0.119	18 93	1.796
07 75	0.301	18 99	2.071
08 02	0.238	19 30	0.286
08 09	0.244	19 59	3.979
08 35	0.195	19 98	2.809
08 59	0.024	20 43	2.904
08 75	0.069	20 77	1.315
08 92	0.008	20 91	0.926
09 22	0.198	21 23	1.297
09 32	0.220	21 62	1.890
09 67	0.903	22 19	3.476
10 12	0.545	22 50	2.323
10 52	0.191	22 93	1.184
10 61	0.052	23 22	0.503
10 73	0.192	23 47	5.117
10 88	2.411	24 02	0.462
11 12	0.428	24 49	3.191
11 54	0.150	24 72	2.161
11 87	0.068	24 87	1.884
12 12	0.080	25 32	1.360
12 49	0.436	25 60	1.460
12 81	0.281	25 78	2.801
12 90	0.102	26 37	2.252
13 23	0.680	26 64	4.306
13 43	0.835	27 09	1.057
13 66	0.467	27 48	1.798
13 97	0.737	28 08	1.252
14 14	0.487	28 22	0.721
14 36	0.378	28 65	0.974
14 73	1.952	29 21	1.226
15 02	0.843	29 76	1.092
15 25	1.583	30 28	0.658
15 61	0.528	30 61	0.362
15 92	1.142	30 92	0.439
16 08	0.872	30 93	0.417
16 42	0.817	31 36	0.432
16 59	2.092	31 90	0.202
		34 76	T
		37 08	T

TABLE 53. BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - Chromosorb 3A (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
08 26	0.010	24 26	1.575
09 79	0.031	24 49	3.490
10 23	0.180	24 78	0.193
10 46	0.228	24 95	3.197
10 68	0.218	25 21	3.020
10 96	0.594	25 50	3.106
11 13	0.616	25 91	2.619
11 34	0.127	26 17	3.854
11 59	0.284	26 59	7.305
11 75	0.198	27 43	3.541
12 03	0.284	27 86	3.023
12 43	0.838	28 40	0.254
12 65	0.238	31 92	0.001
12 86	1.076		
13 14	1.485		
13 33	2.012		
13 61	2.121		
13 81	1.770		
14 07	2.436		
14 80	1.548		
15 02	0.421		
15 21	2.804		
15 71	0.398		
15 93	0.234		
16 31	1.610		
16 84	3.089		
17 40	2.332		
17 95	0.974		
18 13	0.709		
18 45	2.320		
18 99	1.431		
19 45	1.161		
19 99	0.668		
20 39	1.023		
20 97	1.391		
21 28	1.380		
22 13	7.861		
22 49	2.614		
22 70	0.311		
22 95	4.164		
23 29	1.624		
23 50	1.552		
23 73	3.277		
24 05	1.970		

TABLE 54. BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - Chromosorb 3A (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
03 54	0.001	16 20	1.801
03 69	0.253	16 46	1.102
04 10	0.657	16 64	4.338
04 28	0.698	16 96	4.095
05 33	0.013	17 31	1.661
05 46	0.016	17 73	3.186
05 63	0.109	17 92	2.071
05 90	0.013	18 13	3.173
06 75	0.155	18 54	3.370
06 91	0.382	18 73	1.128
07 26	0.206	18 94	2.024
07 53	0.487	19 61	1.175
07 66	0.199	20 01	0.439
07 80	0.517	20 47	1.325
07 95	0.045	20 82	0.501
08 14	0.626	21 31	0.626
08 42	0.170	21 69	0.251
08 79	0.038	22 25	2.396
09.36	0.394	22 57	0.677
09 71	1.269	22 97	1.012
10 16	0.614	23 27	0.092
10 54	0.208	23 55	4.261
10 72	0.132	24 57	5.058
10 94	3.085	25 21	0.428
11 18	0.385	25 37	0.843
11 39	0.101	25 69	4.571
11 71	0.324	26 41	2.524
11 94	0.184	26 71	3.470
12 16	0.147	27 13	0.692
12 38	0.267	27 49	3.895
12 55	0.209	28 13	3.056
12 63	0.173	28 69	0.353
12 88	0.724	29 21	2.486
13 30	1.270	29 77	1.803
13 50	1.302	30 33	0.270
13 75	0.732	30 69	0.366
14 04	1.373	30 89	0.824
14 22	0.528	31 41	0.432
14 46	0.639	31 95	0.118
14 80	3.216	32 45	0.007
15 10	1.220	34 11	0.001
15 32	2.412		
15 78	1.112		
15 90	1.494		

TABLE 55. BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - Chromosorb 1B (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
05 45	0.004	20 41	0.454
06 17	0.064	21 22	0.787
06 97	0.114	21 85	2.500
07 18	0.053	22 06	4.213
07 33	0.038	22 43	1.504
07 48	0.133	22 63	0.802
07 80	0.490	22 87	3.956
08 17	0.586	23 23	1.089
08 35	0.368	23 42	1.029
08 72	0.800	23 66	4.182
09 07	0.613	23 97	1.635
09 64	0.586	24 17	1.388
09 84	0.209	24 41	3.954
10 15	1.355	24 71	0.738
10 41	0.169	24 87	2.173
10 54	0.449	25 13	3.466
10 90	0.906	25 42	2.831
11 06	1.236	25 83	2.794
11 32	0.318	26 09	1.725
11 53	0.899	26 35	1.542
11 72	0.688	26 51	4.380
12 00	0.356	27 17	0.869
12 41	1.423	27 37	1.872
12 52	0.416	27 62	0.826
12 82	1.639	27 83	2.064
13 12	1.895	28 42	0.363
13 31	3.606	31 39	0.001
13 59	3.048	35 92	0.023
13 85	2.604	36 12	0.021
14 04	2.946		
14 24	1.868		
14 55	3.140		
14 78	0.559		
15 02	2.252		
15 23	3.546		
16 36	0.950		
17 44	0.979		
17 97	0.542		
18 15	0.438		
18 46	1.679		
18 98	0.692		
19 42	0.454		
19 87	0.097		
20 35	0.308		

TABLE 56. BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - Chromosorb 1B (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
03 52	0.305	16 12	1.165
03 99	1.107	16 43	0.920
04 16	1.002	16 61	3.748
04 86	0.001	16 95	3.595
05 30	0.006	17 29	1.567
05 47	0.182	17 73	2.618
05 61	0.050	17 91	1.515
05 79	0.062	18 12	2.531
06 00	0.053	18 53	3.239
06 41	1.290	18 94	3.515
06 71	2.057	19 60	2.198
07 12	0.898	20 00	0.705
07 29	0.531	20 21	0.155
07 43	0.908	20 45	0.584
07 58	0.497	22 24	0.169
07 73	1.243	23 56	0.054
07 86	1.454	24 54	0.418
08 06	2.859	24 72	0.391
08 32	3.007	25 36	0.227
08 60	0.528	25 62	0.446
08 73	2.118	25 80	0.938
09 32	3.032	26 38	0.969
09 67	3.846	26 66	1.884
10 19	3.050	27 52	0.039
10 62	1.665	28 12	0.052
10 89	8.949	30 62	0.014
11 12	1.962	30 94	0.080
11 64	1.216	33 00	0.013
11 86	0.688	34 46	0.001
12 14	0.455		
12 41	1.577		
12 58	0.750		
12 80	1.380		
13 24	1.690		
13 44	2.005		
13 66	1.219		
13 98	1.811		
14 15	0.360		
14 37	0.988		
14 74	3.604		
15 04	1.348		
15 25	2.282		
15 64	0.816		
15 86	1.397		

TABLE 57. BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - Chromosorb 3B (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
04 36	0.115	21 85	2.824
04 57	0.102	22 08	4.776
05 51	0.009	22 46	1.829
06 30	0.006	22 65	1.785
07 37	0.023	22 90	4.782
07 46	0.022	23 26	2.031
07 65	0.057	23 45	1.795
07 89	0.109	23 69	4.477
08 28	0.205	24 01	2.780
08 42	0.097	24 21	1.286
08 82	0.248	24 44	4.601
09 16	0.316	24 74	1.385
09 33	0.104	24 90	2.245
09 71	0.367	25 17	3.967
09 93	0.255	25 45	2.352
10 20	0.873	25 59	0.918
10 59	0.579	25 86	3.506
10 97	0.459	26 12	1.875
11 11	0.619	26 38	1.509
11 36	0.244	26 54	5.134
11 57	0.830	27 18	3.557
11 77	0.441	27 60	0.618
11 97	0.271	27 91	3.362
12 42	0.726	28 41	2.727
12 65	0.115	29 01	2.234
12 86	0.740	29 59	1.570
13 15	0.564	30 17	1.195
13 34	0.973	30 73	0.762
13 63	0.958	31 23	0.482
13 82	0.699	31 77	0.233
14 07	0.805	32 26	0.045
14 81	0.570		
15 03	0.149		
15 22	0.964		
15 72	0.170		
15 94	0.094		
16 31	0.666		
16 83	1.326		
17 35	1.400		
17 97	0.569		
18 03	0.463		
18 36	1.309		
18 91	1.022		
19 36	1.024		
19 90	0.818		
20 32	1.338		
21 22	3.269		

TABLE 58. BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - Chromosorb 3B (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
03 67	0.049	19 64	15.164
04 07	0.167	20 03	1.311
04 23	0.154	20 49	1.971
06 36	0.009	20 84	0.911
07 00	0.238	21 05	0.114
07 17	0.076	21 29	0.982
07 62	0.010	21 67	1.079
07 79	0.028	22 28	2.906
07 93	0.017	22 62	11.664
08 09	0.163	23 00	1.847
08 76	0.003	23 30	0.581
09 32	0.244	23 56	5.410
09 66	0.655	24 62	5.812
10 17	0.546	25 23	0.987
10 58	0.293	25 40	1.061
10 86	1.329	25 70	1.320
11 09	0.296	25 85	2.374
11 57	0.193	26 44	1.953
11 81	0.066	26 73	3.346
12 05	0.003	27 17	1.088
12 42	1.169	27 53	1.936
12 75	0.194	28 16	1.572
13 18	0.366	28 50	0.634
13 40	0.483	28 71	0.178
13 60	0.243	28 85	0.411
13 92	0.437	29 24	1.387
14 18	0.659	29 81	0.933
14 53	0.464	30 04	0.412
14 67	1.621	30 45	0.493
15 00	0.547	30 68	0.645
15 24	0.779	31 02	1.220
15 61	0.298	31 42	0.831
15 83	1.217	32 00	0.850
16 22	0.818	34 36	T
16 42	0.271	36 24	0.005
16 60	1.369		
16 72	0.383		
16 94	1.544		
17 30	0.797		
17 49	0.496		
17 73	1.241		
17 91	0.751		
18 14	1.441		
18 56	1.838		
19 03	2.644		

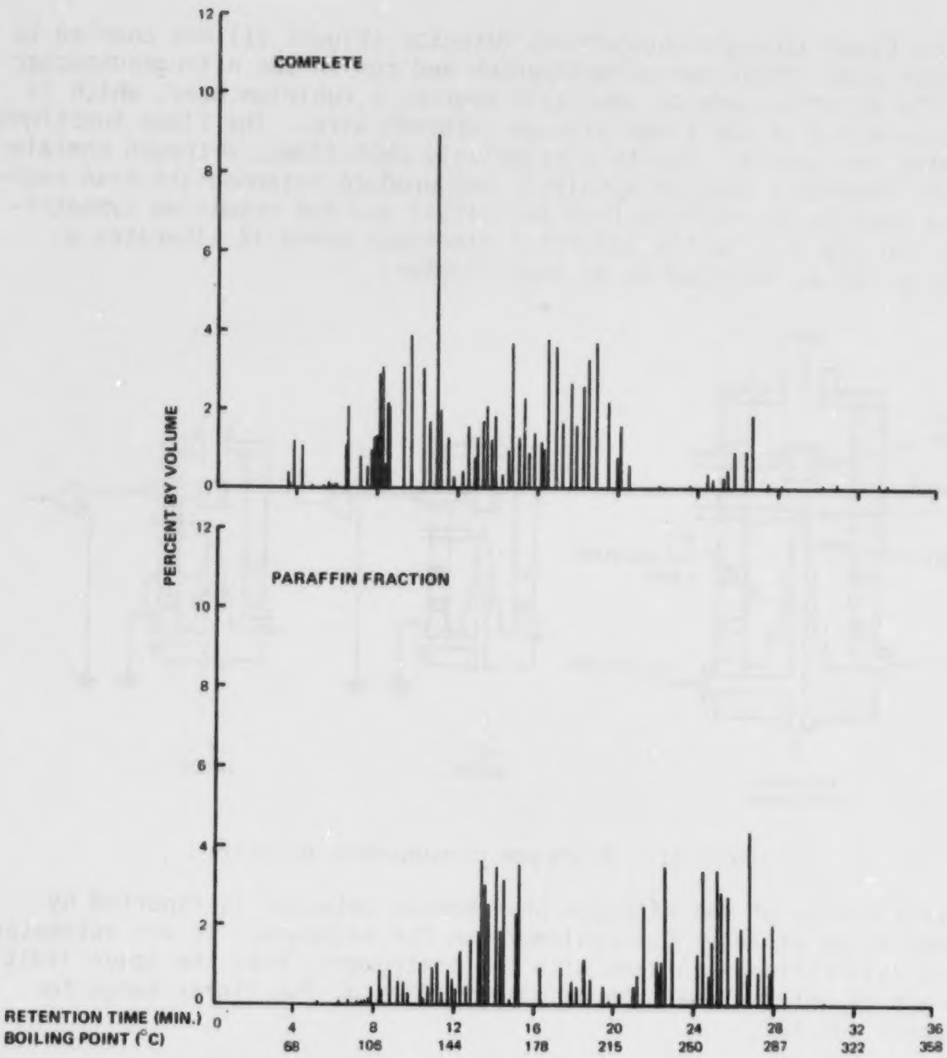


Figure 30. Graphic representation of boiling point distribution tables 55 and 56, idle power point using high sulfur fuel.

Nitrosamine Analyses

Two analyses for nitrosamines were made of the extracted fraction of exhaust particulates using a Perkin Elmer nitrogen-phosphorous detector. The samples were taken at idle and climb power settings using low sulfur fuel.

The nitrosamines were extracted from the teflon filters and isolated in the dichloromethane fraction (10 ml) using the procedure described in EPA 650/2-75/056.

A Perkin Elmer nitrogen-phosphorous detector (Figure 31) was coupled to a Perkin Elmer model 3920B gas chromatograph and run in the nitrogenphosphorous mode. The detector uses as an alkali source, a rubidium bead, which is heated independently of the flame with an internal wire. The flame functions only to ionize the sample. Due to a relatively cool flame, nitrogen containing compounds undergo a partial pyrolysis and produce intermediate cyan radicals. These take up an electron from the alkali and the resulting symmetrical cyanide ion migrates to the collector electrode where it liberates an electron which can be detected by an electrometer.

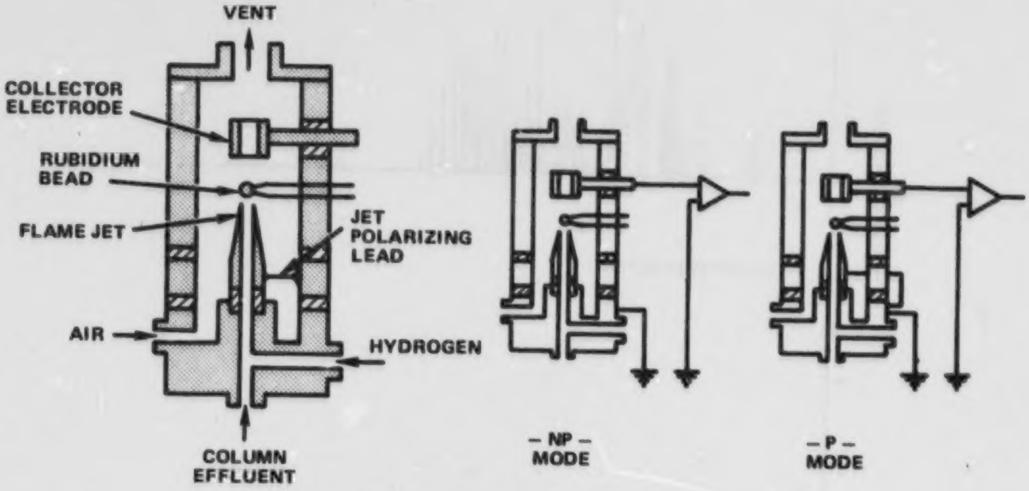


Figure 31. Nitrogen phosphorous detector.

The sensitivity of the nitrogen-phosphorous detector is reported by Perkin-Elmer to be at least 0.5 coulomb/gram for nitrogen. It was estimated, while using calibration standards with the instrument, that the lower limit for compounds of interest was approximately 10^{-13} g. The linear range for the instrument was 10^{5}.

The following conditions were observed during calibration and sample runs.

Column: 6' x .125" 10% Carbowax 1540 (polyethylene glycol, molecular weight 1300-1600) on ABS (acid and alcoholic base washed and silanized diatomaceous earth), 60-70 mesh
Detector temp.: 165°C
Injector temp.: 165°C
Column temperature program: 117°C/8 min./8°C rate/165°C/16 min.
Detector bead setting: 5.40
Helium carrier: 17 ml/min., 93 psi
Hydrogen: 3 ml/min., 7.5 psi
Air: 100 ml/min., 44 psi

A 1 ul injection of dichloromethane extract was analyzed to determine if nitrosamine interferences might be present. None were observed.

A 0.2 ul injection of a nitrosamine standard containing 0.05 ng each of dimethylnitrosamine, diethylnitrosamine, diisopropylnitrosamine and dibutylnitrosamine was analyzed. Retention times, peak heights, and divisions per pg are noted below.

Compound	Retention Time, Min.	Peak Height Divisions	Sensitivity, div/pg
DMA	5.5	15.8	316.0
DEA	7.7	12.0	240.0
DIA	12.2	9.0	180.0
DBA	16.3	5.5	110.0

Nitrosamines were not found to be present at either idle or climb power settings using the instrumentation and detection methods described above. If nitrosamines are present, they are below the 10^{-13} g detection limit of the instrumentation.

Phenol Analyses

In addition to the analysis of the organic fraction of engine exhaust particulate material for polynuclear aromatic compounds, the analysis for phenols was also undertaken. Phenolic compounds, although not necessarily carcinogenic themselves, have a synergistic effect in conjunction with certain polynuclear hydrocarbons. The phenols have a tendency to make these polynuclear compounds much more carcinogenic than they would be alone. Two samples of exhaust particulate were taken on teflon filters. The power conditions for these samples were idle and climb out, and the fuel used was the low sulfur type. The extraction of the phenolic compounds was performed in accordance with the procedure given in EPA 650/2-75/056.

As a result of using the prescribed extraction techniques, the phenols were taken up finally in diisopropylether (DIE). A one microliter aliquot of this solution was injected into a gas chromatograph for analysis. Prior to this step a calibration procedure was used to ascertain retention times and sensitivity of six common phenol type compounds. To account for possible interferences a blank was produced by using the extraction technique on an unexposed filter.

Six phenol compounds were dissolved in DIE each at a concentration in the final solution of 17 ng/ul. The phenols used in this calibration were phenol, o-cresol, m-cresol, p-cresol, 2, 6-dimethyl phenol and salicylaldehyde. The analysis was performed on a Perkin Elmer Model 3920B gas chromatograph using the following conditions.

Column: 6' x 0.125" stainless steel column packed with, 10% OV-3 (silicones with 10% phenyl) + 1% FFAP (free fatty acid phase Carbowax 20M reacted with nitroterephthalic acid; Carbowax 20M is polyethylene glycol of average MW 15000-20000) on gas Chrom. Q (acid and alcoholic base washed and silanized diatomaceous earth), 80/100 mesh.

Carrier gas: Helium, flow 70cc/min @ 93 psi

Detector: flame ionization detector, hydrogen fuel (28 psi) air oxidant (48 psi)

Temperatures: Oven: 105°C isothermal
Injection Port: 160°C
Detector: 150°C

Using the gas chromatograph, under the conditions described above the retention times and sensitivities of the six phenols were obtained as shown in Table 59.

TABLE 59. RETENTION TIME AND SENSITIVITY OF PHENOLS

Compound	Retention Time, Min	Sensitivities (Div/ng) (Peak-Height)
Salicylaldehyde	5.8	4.27
2, 6-Dimethylphenol	11.8	3.22
Phenol	12.8	2.87
o-Cresol	14.6	3.34
m-Cresol	20.3*	4.09
p-Cresol	20.3*	-

* m and p - Cresols could not be separated.

A chromatogram of this mixture showing five peaks that represent the six phenols (m and p cresol did not separate) is shown in Figure 32. A chromatogram of a typical sample (IA) is shown in Figure 33.

The chromatographic analysis of the two samples (idle and climb out, using low sulfur fuel) showed various peaks but only phenol could be identified positively from its retention time. About 4 ng of phenol was found in the idle sample and about 1.3 ng was in the climb out sample. The concentration of phenol in the exhaust gas sampled was calculated to be approximatly 0.15 ng/m^3 and 0.047 ng/m^3 for idle and climb out respectively.

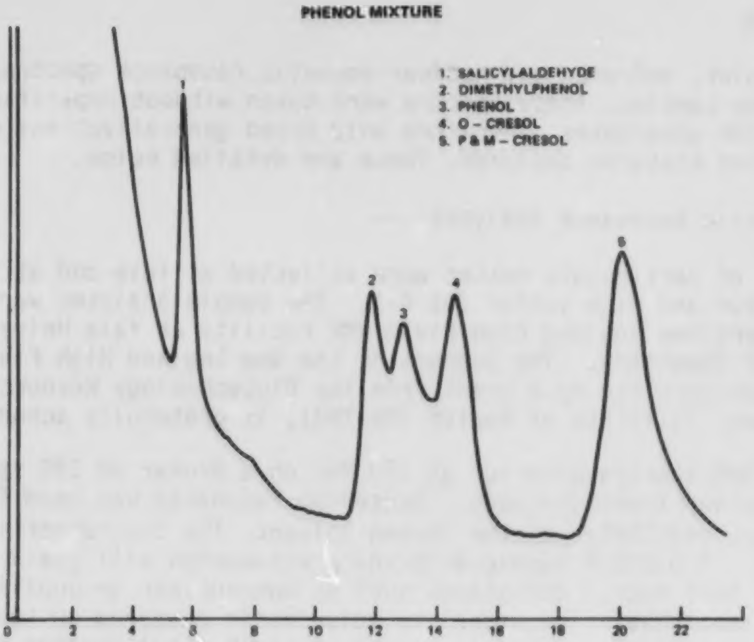


Figure 32. Chromatogram of mixture of phenols.

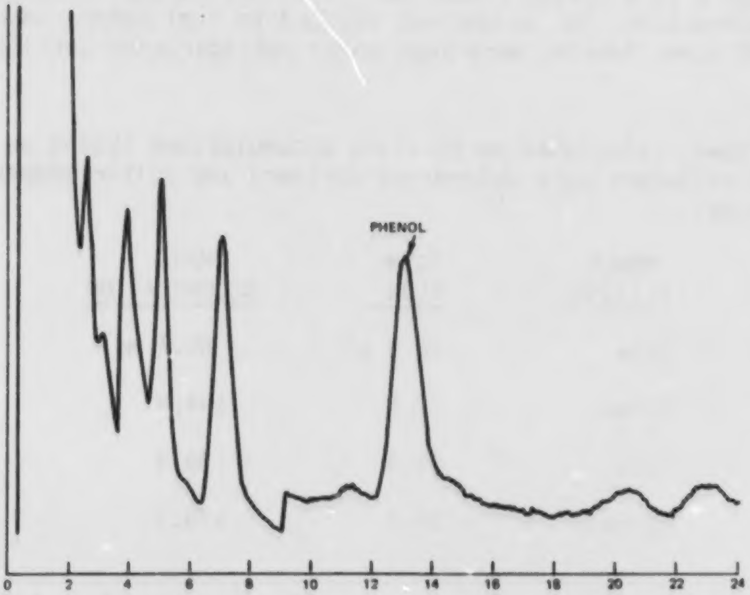


Figure 33. Chromatogram of typical exhaust sample.

Spectral Data

Ultraviolet, infrared and nuclear magnetic resonance spectra were taken on some of the samples. These spectra were taken without separation of the extracts of the adsorbates. Therefore only broad generalizations can be made for the complex mixtures analyzed. These are detailed below.

Nuclear Magnetic Resonance Analyses---

Samples of particulate matter were collected at idle and at climb using both low sulfur and high sulfur Jet A-1. The sample analyses were conducted at the Southern New England High Field NMR Facility at Yale University's Department of Chemistry. The support of the New England High Field NMR Facility, made possible by a grant from the Biotechnology Resources Program of the National Institute of Health (RR-798), is gratefully acknowledged.

Proton NMR spectra were run at 270 MHz on a Bruker HX 270 spectrometer using the Fourier transform mode. Deuterium resonance was used for a field/frequency lock and $CDCl_3$ was the chosen solvent. The instrument is extremely sensitive. A 0.001 M sample with sharp resonances will yield adequate spectra in a half hour. Operations such as homonuclear decoupling and integration are available. The signal to noise ratio measured on the highest peak of the quartet in a one pulse spectrum of 1% ethyl benzene is 120:1.

The organic fraction of the particulate samples was extracted using $CDCl_3$ as the solvent in a Soxhlet extractor. The resulting solution was passed through a 10 u teflon filter to remove any particulates carried over during the extraction. The volume was reduced to 1 ml before insertion into a 5 mm O.D. NMR tube. Samples were kept under refrigeration until analysis.

Total flows, calculated particulate accumulations (based on flow and estimated mass emissions data determined earlier) and filter temperatures are tabulated below:

SAMPLE	POWER SETTING	TOTAL FLOW	MASS ACCUMULATION	FILTER TEMPERATURE
1A	Idle	26.3 m^3	80.7 mg	113°F
3A	Climb	27.8	194.9	135
1B	Idle	29.3	89.9	149
3B	Climb	39.7	278.3	139

In addition to the sample spectra, a 20 ul sample of each fuel in $CDCl_3$ was run to document any possible differences.

The spectra obtained appear to delineate three general regions. The aromatic region, about 7 to 8 ppm (delta shift) is well defined. For the purposes of general data interpretation, a delta shift of 0 to 2.5 ppm will be defined as being largely aliphatic in nature. Those shifts lying between the aliphatics and the aromatics will be defined as having olefinic character. With these suppositions in mind, the following Table 60 was generated which lists integration counts normalized to 2000 scans. Note that 0.2 mg benzo (a) pyrene yields 90 counts when normalized to 2000 scans. This gives a rough correlation between integration counts and the amount of material present.

Table 60 shows the integrated reponse of groups designated aromatic, aliphatic, and olefinic in integration counts per cubic meter of sample gas and can be used as an approximation of the amount of material present.

TABLE 60. NMR INTEGRATED RESPONSE /m^3

Sample	Aromatic(1)	Aliphatic(2)	Olefin(3)	Total
1A Idle	0.836	7.300	3.042	11.178
3A Climb	0.252	7.554	2.806	10.612
1B Idle	5.666	7.167	2.321	15.154
3B Climb	0.605	4.811	0.957	6.373

(1) Delta shift 7-8 ppm
(2) Delta shift 0-25 2.5 ppm
(3) Delta shift 2.5-7 ppm
(4) Integrated response per mg BAP is 450

Table 61 is an adjustment of the NMR response on a hydrocarbon basis. If C_8H_7 is assumed a representative aromatic, $C_{10}H_{20}$ a representative olefin, and $C_{10}H_{22}$ a representative aliphatic, the adjusted distribution of counts per cubic meter of sample gas is as described.

TABLE 61. NMR RESPONSE - HYDROCARBON BASIS

Sample	Aromatic (as C_8H_7)	Aliphatic (as $C_{10}H_{22}$)	Olefin (as $C_{10}H_{20}$)	Total
1A Idle	12.30	47.16	21.29	80.75
3A Climb	3.71	48.80	19.64	72.15
1B Idle	83.37	46.30	16.25	145.92
3B Climb	8.90	31.08	6.70	46.68

Table 62 expresses adjusted counts per cubic meter of sample on a percent hydrocarbon basis. Jet A-1 is included for comparison purposes. This table serves as a qualitative assessment of the hydrocarbon distribution at each power setting sampled.

TABLE 62. PERCENT HYDROCARBON BASIS

Sample	Aromatic	Aliphatic	Olefin
1A Idle	15.23	58.40	26.37
3A Climb	5.14	67.64	27.22
1B Idle	57.13	31.73	11.14
3B Climb	19.07	66.58	14.35
Jet A-1	12.08	82.89	5.30

Figures 34 through 39 show the actual NMR spectra obtained for typical samples: samples from low sulfur at idle and climb, samples from high sulfur at idle and climb, and low and high sulfur Jet A-1 fuels.

Both the high sulfur and low sulfur idle samples were divided into five equal fractions each and were brought to 1/2 ml volume. To four of these samples was added approximately 50 ug anthracene, pyrene, fluoranthene and phenanthrene, respectively. This resulted in two groups of samples whose only difference was a measured quantity of known contaminant.

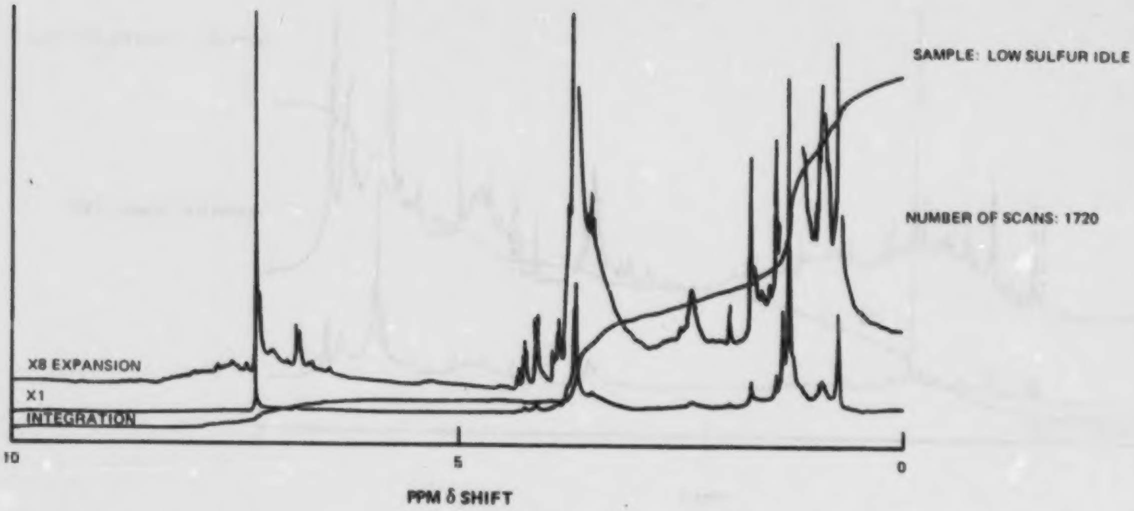


Figure 34. Nuclear magnetic resonance - low sulfur idle.

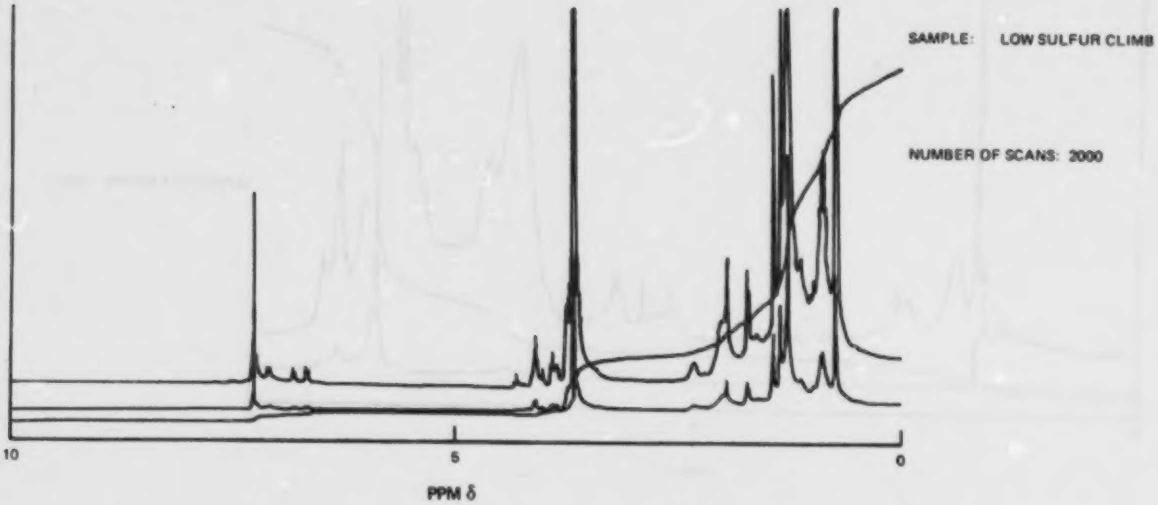


Figure 35. Nuclear magnetic resonance - low sulfur climb.

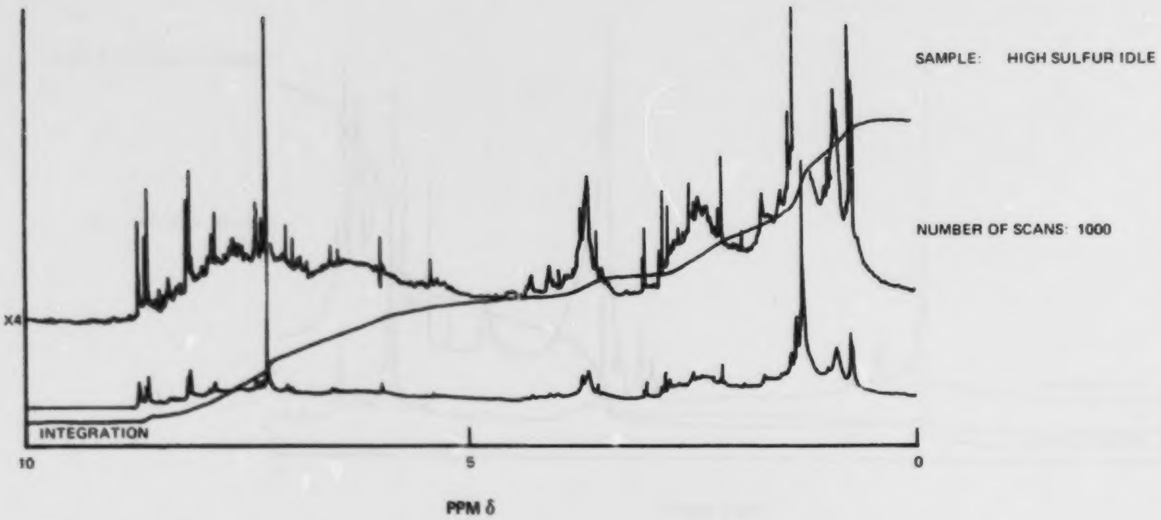


Figure 36. Nuclear magnetic resonance - high sulfur idle.

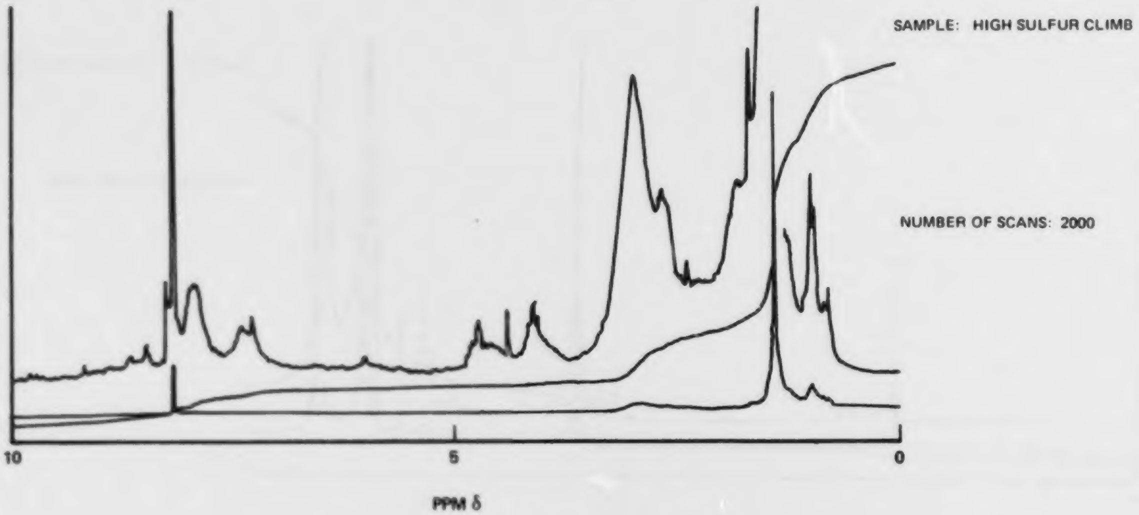


Figure 37. Nuclear magnetic resonance - high sulfur climb.

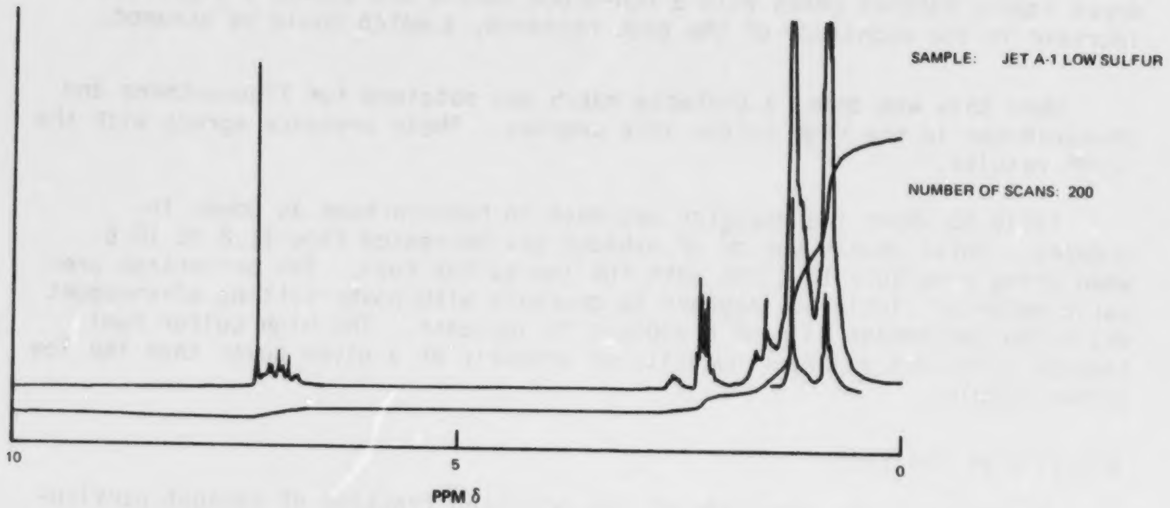


Figure 38. Nuclear magnetic resonance - Jet A-1 low sulfur.

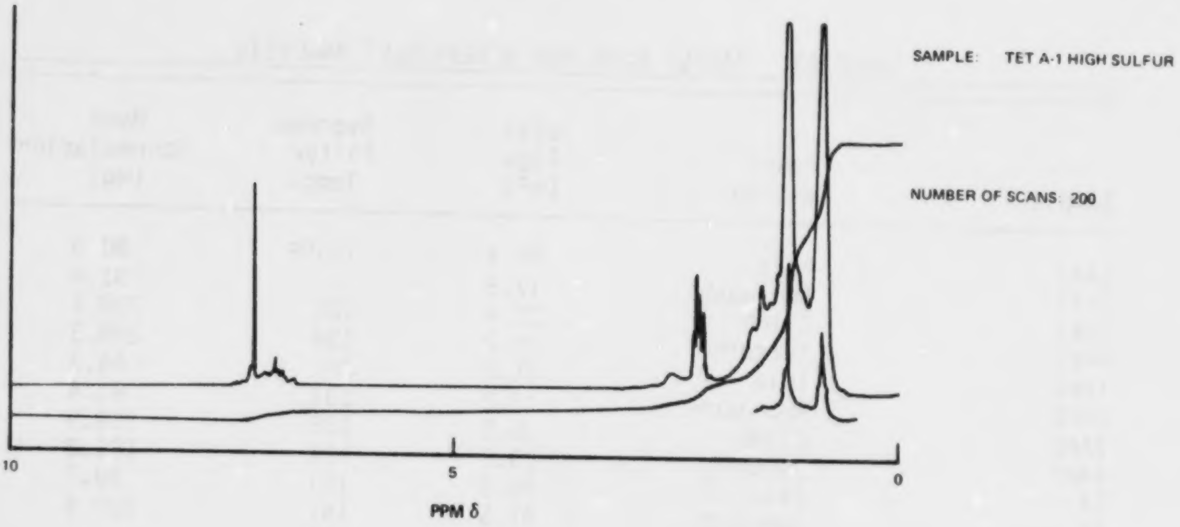


Figure 39. Nuclear magnetic resonance - Jet A-1 high sulfur.

Spectra were obtained for each of the above groups using identical run parameters within each group so they could be overlayed and compared. If a doped sample matched peaks with a non-doped sample and showed a significant increase in the magnitude of the peak response, a match could be assumed.

When this was done, a probable match was obtained for fluoranthene and phenanthrene in the high sulfur idle samples. Their presence agrees with the GC/MS results.

Table 60 shows the expected decrease in hydrocarbons as power increases. Total counts per m^3 of exhaust gas decreased from 11.2 to 10.6 when going from idle to climb with the low sulfur fuel. The percentage aromatic material (Table 62) appears to decrease with power setting advancement while the percentage aliphatic appears to increase. The high sulfur fuel samples contained a larger quantity of aromatic at a given power than the low sulfur samples.

Ultraviolet Analyses---

Twelve UV scans were made of the extracted fraction of exhaust particulates collected from twelve exhaust samples. Total sample flow, average filter surface temperature, and calculated mass accumulation (based on total flow and estimated from mass emissions data) are given in Table 63.

TABLE 63. SAMPLE DATA FOR ULTRAVIOLET ANALYSIS

Sample	Power Setting	Total Flow (m^3)	Average Filter Temp.	Mass Accumulation (mg)
1A#1	Idle	26.4	125°F	80.8
2A#1	Approach	17.5	-	81.4
3A#1	Climb	32.4	124	230.7
4A#1	Takeoff	32.2	139	248.3
1A#2	Idle	21.0	107	64.3
2A#2	Approach	13.2	133	61.4
3A#2	Climb	36.5	128	259.9
4A#2	Takeoff	23.5	119	181.2
1B	Idle	29.3	150	89.7
2B	Approach	47.5	161	220.9
3B	Climb	-	154	-
4B	Takeoff	42.7	142	329.2

The organic fraction was removed from the particulates using a Soxhlet extractor and n-hexane as the solvent. The solvent was chosen for its ability to dissolve most of the collected organic material and its freedom from interfering peaks when injected into the liquid chromatograph. The above samples are identical with those used for the liquid chromatograph analysis. The UV sample runs were made after completion of the liquid chromatography runs. All samples were brought to 3 ml volume to accommodate a 1 cm cell.

Ultraviolet and visible spectra were run on a Varian 635D spectrophotometer at a slit width of 0.5 nm and a scan speed of 100 nm per minute. Scans were made from 800 through 200 nm. Cells were Suprasil with a useable wavelength of 165 to 2600 nm. All engine sample runs were made with n-hexane as the reference in the double beam mode.

Figures 40, 41, 42, and 43 show the UV absorption spectra of hexane, undecane, fluoranthene and a mixture of 16 polynuclear aromatic hydrocarbons. The aliphatic compounds show absorptions at around 230 and 270 nm; the polynuclear compounds show absorptions at 410 and 435 nm with a broad band of high intensity between 220 and 380 nm.

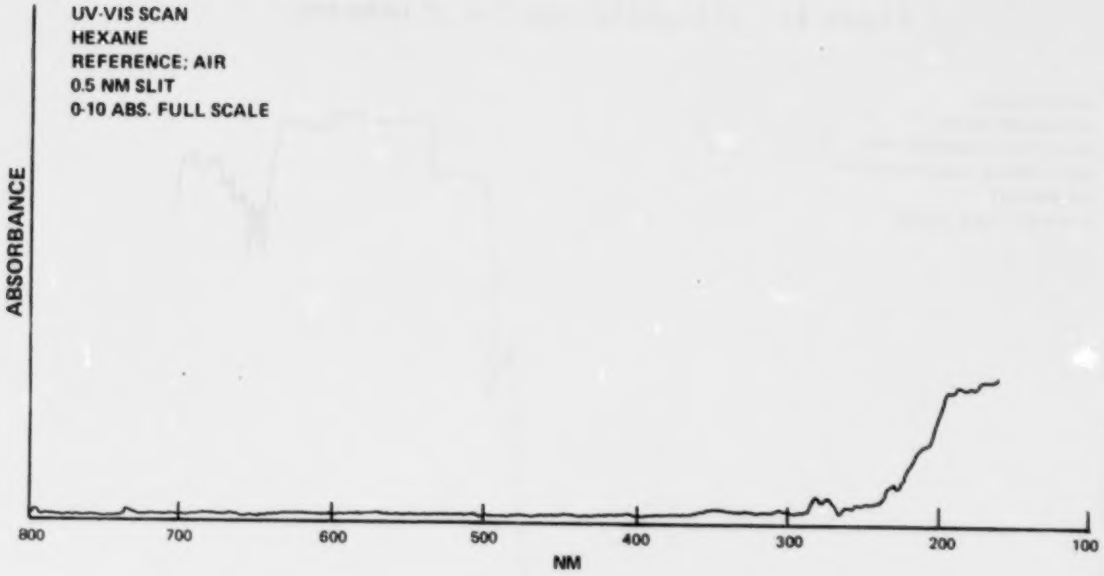


Figure 40. Ultraviolet spectra of hexane.

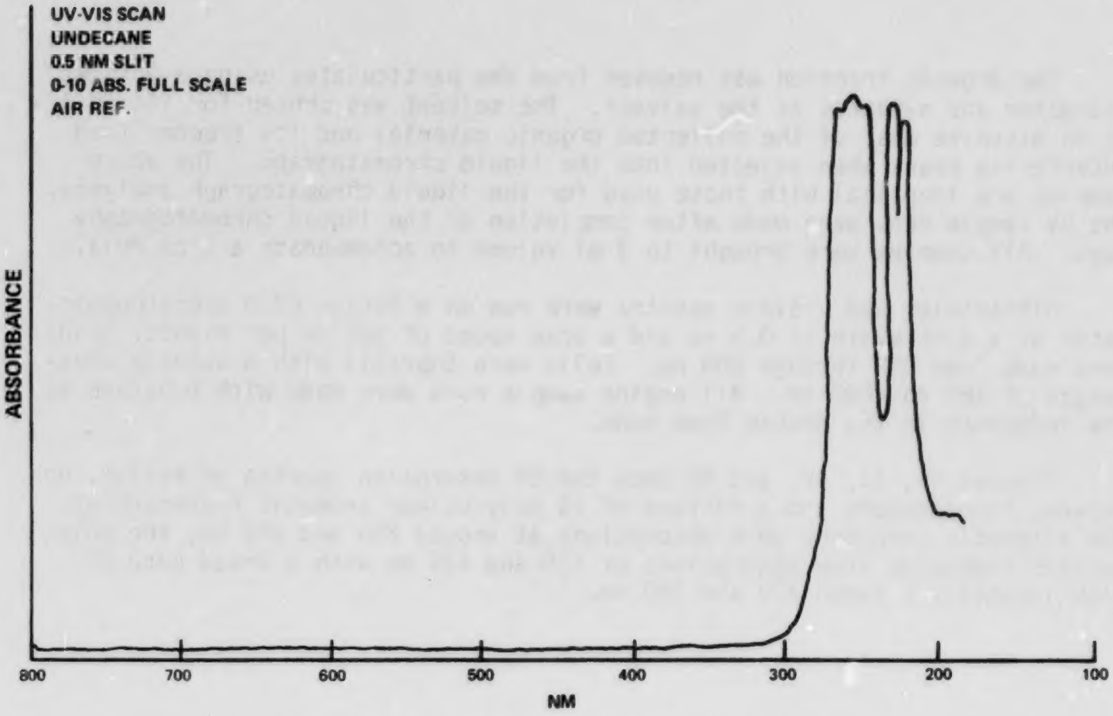


Figure 41. Ultraviolet spectra of undecane.

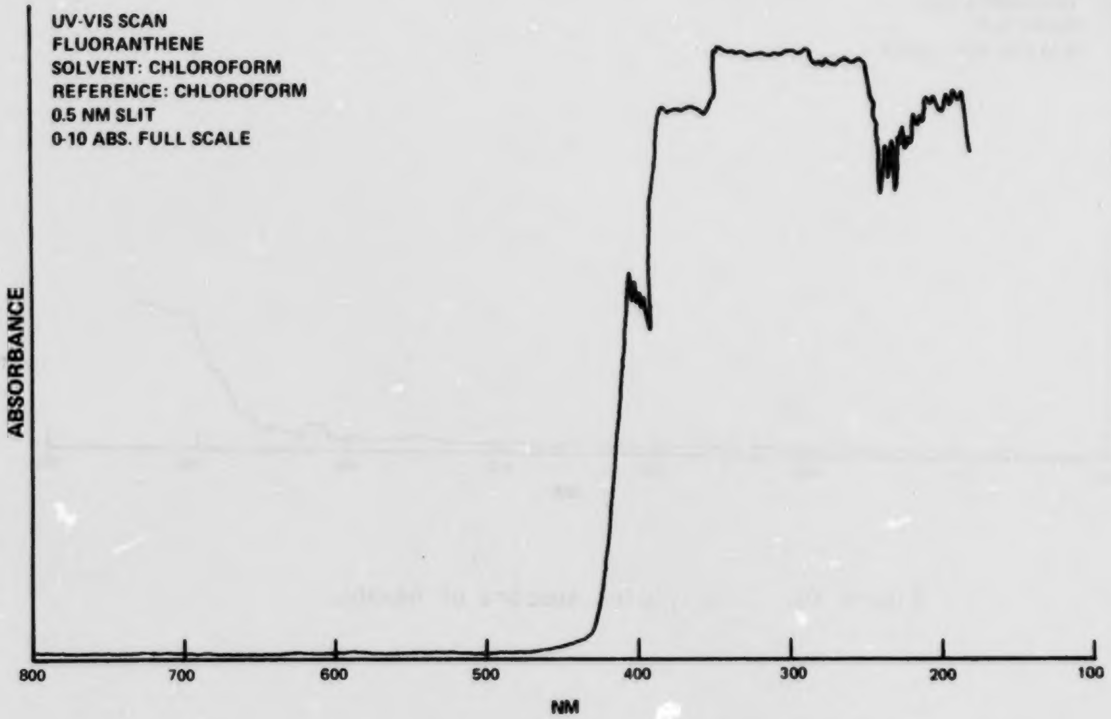


Figure 42. Ultraviolet spectra of fluoranthene.

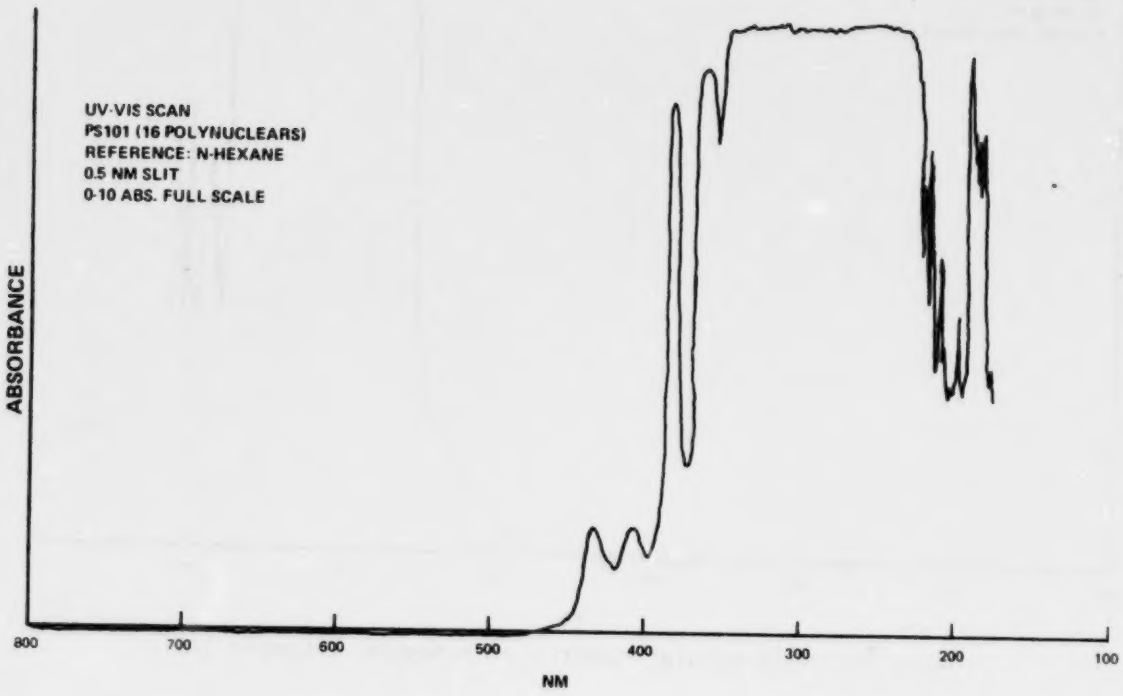


Figure 43. Ultraviolet spectra of 16 polynuclears in n-hexane.

Spectra of exhaust samples show broad absorption bands between 220 and 320 nm from idle, low sulfur samples with the general trend to lower absorption intensities and lower wavelengths as power increases and as fuel is changed from low sulfur to high sulfur. These trends suggest a lowering of aromatic/PAH content. Figures 44, 45, 46, 47, and 48 show representative examples for sample 1A #1, sample 3A #1, sample 1B, sample 2B, and sample 4B, respectively.

Sample 1A#1 from idle power, low sulfur, showed a much higher UV absorption and at higher wavelengths than sample 3A#1 climb power, low sulfur. This confirms the decrease in PNA/aromatic content as power increases as evidenced by higher UV absorptions and higher wavelengths with decrease in power. The B samples compared to the A samples (specifically 1B and 1A#1) show a similar trend of decrease in PNA/aromatics with increase in sulfur content.

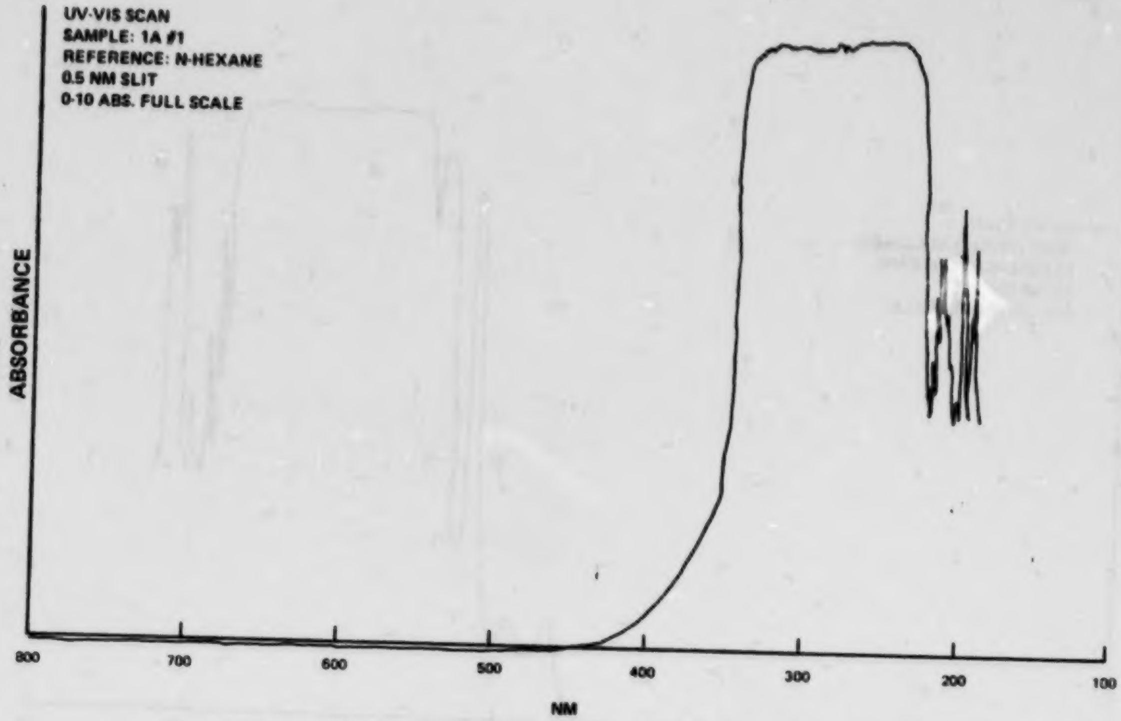


Figure 44. Ultraviolet spectra of n-hexane - sample 1A#1.

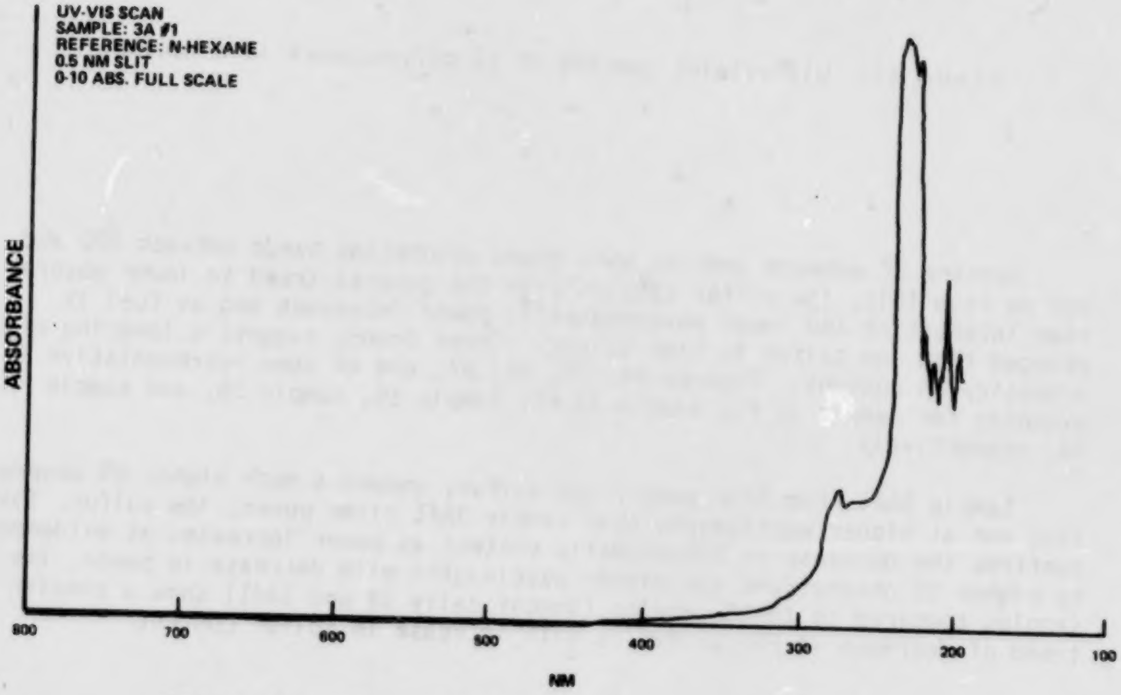


Figure 45. Ultraviolet spectra of n-hexane - sample 3A#1.

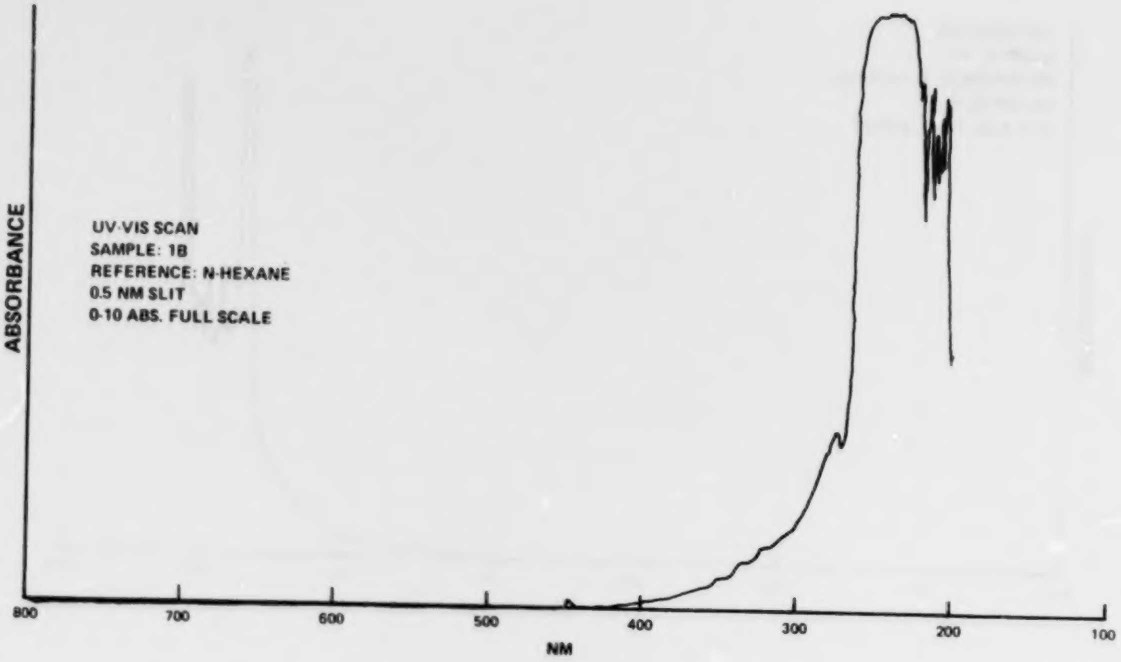


Figure 46. Ultraviolet spectra of n-hexane - sample 1B.

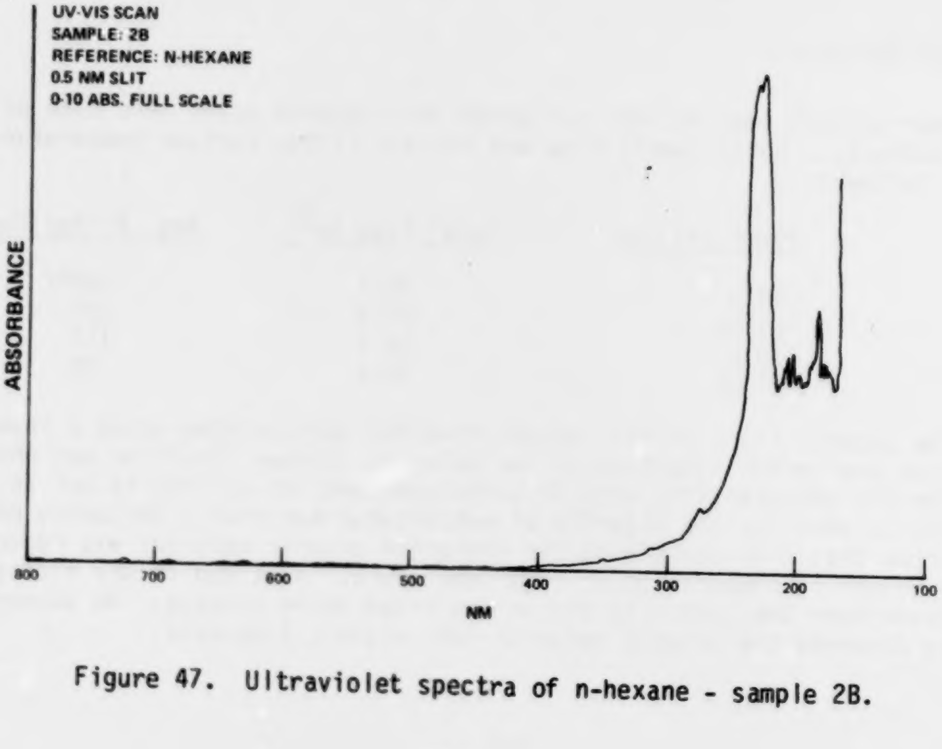


Figure 47. Ultraviolet spectra of n-hexane - sample 2B.

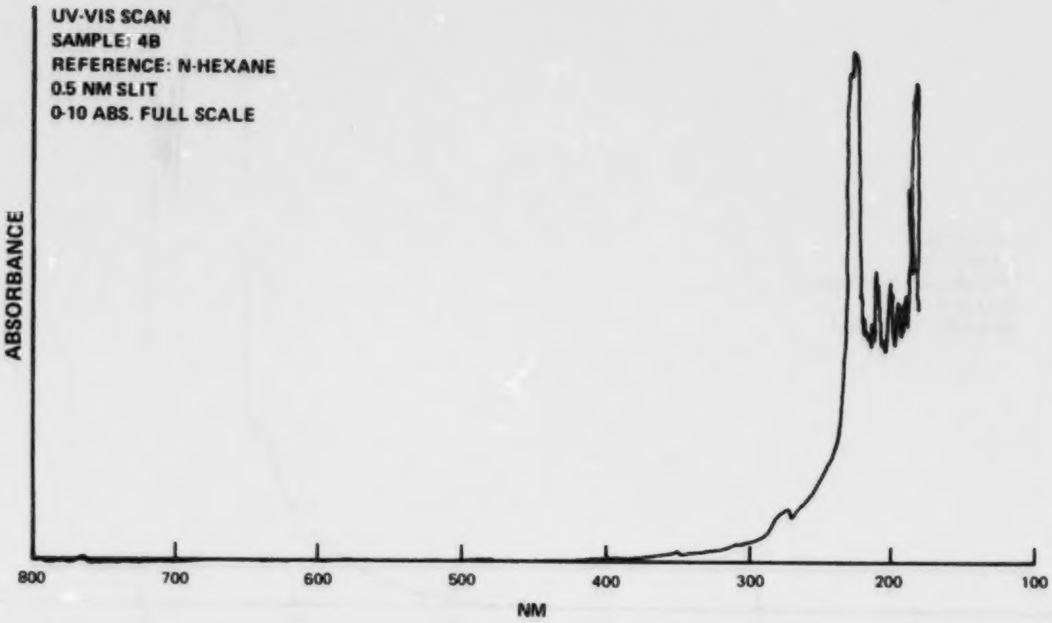


Figure 48. Ultraviolet spectra of n-hexane - sample 4B.

Infrared Analysis---

Four exhaust samples were collected and infrared scans were made of their extracts. Total sample flow and average filter surface temperature are as follows:

Sample	Power Setting	Total Flow (m^3)	Avg. Filter Temp.
1A	Idle	26.4	109°F
3A	Climb	27.8	120
1B	Idle	29.4	117
3B	Climb	42.4	126

The organic fraction was removed from the particulates using a Soxhlet extractor and carbon disulfide as the solvent. Carbon disulfide was chosen both for its compatability with IR techniques and its ability to act as a suitable solvent for the majority of extractable material - including PAH. The carbon disulfide containing the extracted organic material was reduced to a 1 ml volume by evaporation at room temerature. A stream of dry nitrogen was passed over the sample to aid in the evaporation process. No attempt was made to separate the organic material into organic fractions.

Scans were made using both a Beckman IR20A and a Perkin-Elmer model 283 spectrophotometer. The frequency scanned was 4000 to 600 (CM^{-1}). A sealed cell with 0.5 mm path length was used for each of the extracted particulate samples. A 0.1 mm cell was used in producing an IR scan of both the low sulfur and high sulfur Jet A-1 fuel. The instruments were run double bean with carbon disulfide as the reference for the extracts of the particulate samples and air as the reference for the fuel samples.

The detectable limit of the IR20A was determined as 0.3 mg/ml using pyrene. No major peaks could be discerned from baseline noise below this level. It was concluded that a total of organic materials considerably more than 0.3 mg/ml would be necessary to achieve sufficient response from the instrument to identify specific functional groups in complex mixtures.

All spectra show the expected presence of aliphatic, olefinic, and aromatic material. The aromatic and olefin indication of all exhaust samples was less than present in the starting fuels. A carbonyl at approximately 1730 cm^{-1} is also evident in the 3A and 3B samples, especially 3B.

The IR spectra of the two fuels show no significant differences. On the basis of IR scans, the fuels can be considered to be the same.

Based on the limited number of exhaust samples analyzed, no other correlation can be made regarding effect of power setting and fuel used.

Representative IR spectra are shown in Figures 49, 50, 51, and 52 for an aromatic, fluoranthene; an aliphatic, undecane; the starting fuel and a exhaust sample (3A) showing the carbonyl.

Fuel Analysis

The fuel used in this test was a common aircraft turbine engine fuel whose designation in Canada is JP-1 (Jet A-1 in the U.S.).

The fuel was subjected to various types of analyses to ascertain sulfur content, aromaticity, boiling point distribution and PAH content. The fuel was found to contain 0.0065% sulfur by weight. The boiling point distribution was carried out by separating the paraffins from the olefins and aromatics using ASTM method D-1319-70. This paraffin fraction and the complete fuel were analyzed for boiling point distribution using ASTM method D-2887-73. Analysis for PAH concentration was performed by A. D. Little, Inc. and Radian Analytical Labortories, Inc. using gas chromatograph-mass spectrometric techniques.

The results of the sulfur analyses are included in the section on sulfur analyses of the exhaust. The analyses clearly establish that we were able to dope the standard fuel successfully to get a high sulfur content fuel as required.

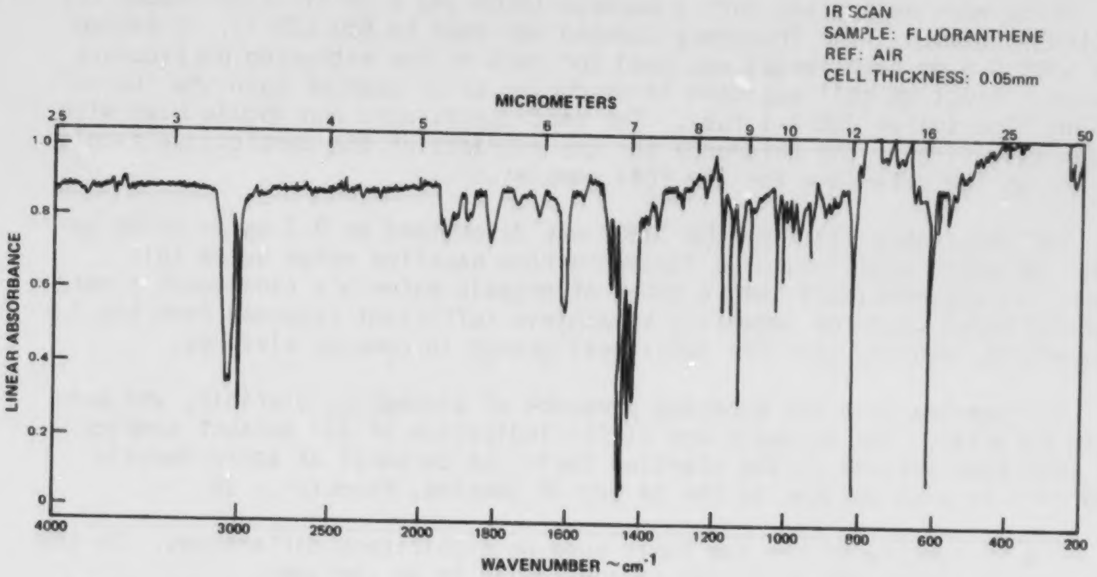


Figure 49. Infrared analysis of fluoranthene.

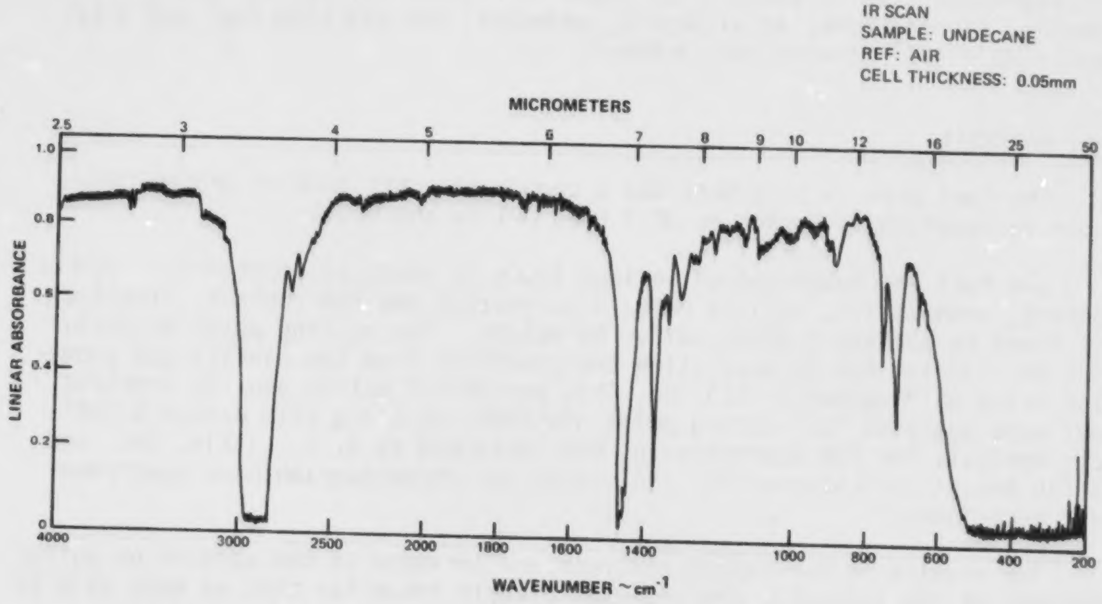


Figure 50. Infrared analysis of undecane.

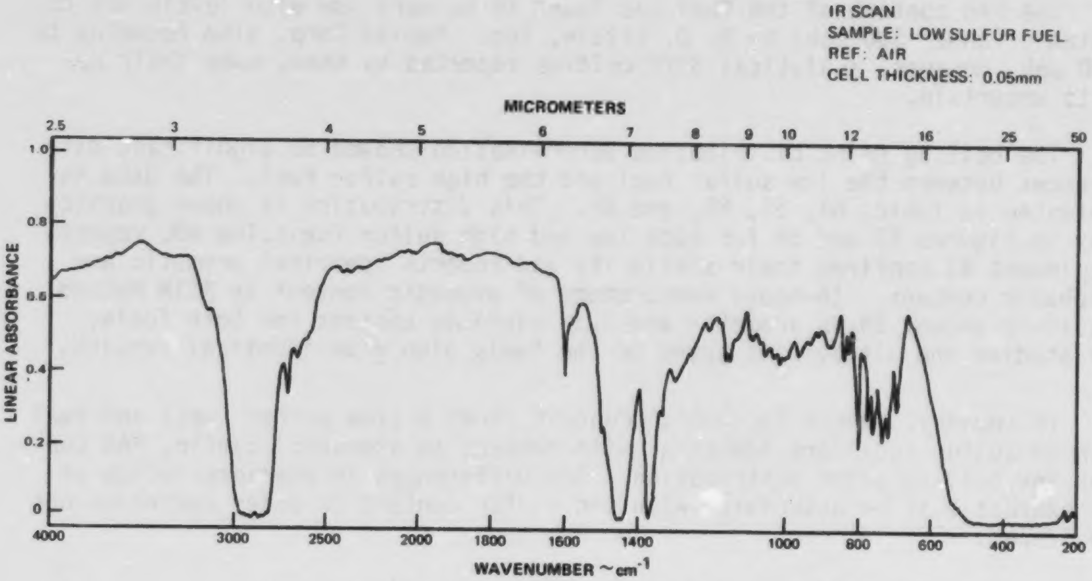


Figure 51. Infrared analysis of low sulfur fuel.

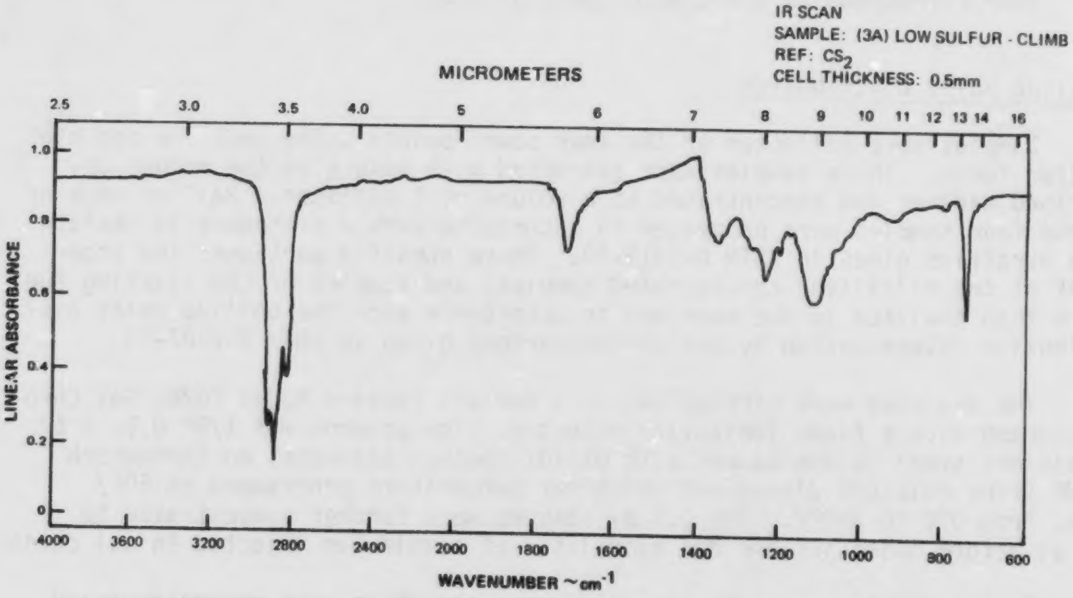


Figure 52. Infrared analysis of low sulfur climb sample.

The PAH content of the fuel was found to be very low with levels not detectable (under 500 ppb) by A. D. Little, Inc. Radian Corp. also found up to 3000 ppb. However, analytical difficulties reported by them, make their results uncertain.

The boiling point distribution determination showed no significant differences between the low sulfur fuel and the high sulfur fuel. The data is presented in Tables 64, 65, 66, and 67. This distribution is shown graphically in Figures 53 and 54 for both low and high sulfur fuels.The ADL report supplement #1 confirms their similarity and reports identical aromatic and aliphatic content. In-house measurement of aromatic content by ASTM Method D-1319-70 showed 19.9% aromatic and 0.3% olefinic content for both fuels. NMR studies and ultraviolet scans of the fuels also gave identical results.

In summary, except for sulfur content, fuel A (low sulfur fuel) and fuel B (high sulfur fuel) are identical with respect to aromatic, olefin, PAH content and boiling point distribution. Any differences in characteristics of the exhaust must be associated with the sulfur content or other variables not considered.

The fuel analysis provided by the EPA is as follows:

low sulfur fuel	84.16%C, 14.96%H
high sulfur fuel	84.01%C, 14.97%H

Both correspond to a H:C mole ratio of 2.12

Boiling Point Distribution

Samples were collected at the four power points using both low and high sulfur fuels. These samples were extracted with hexane in the manner described earlier and concentrated to a volume of 1 milliter. Half of each of these four samples were processed in accordance with a procedure to isolate the paraffins given in ASTM D-1319-70. These paraffin portions; the other half of the milliliter concentrated samples; and samples of the starting fuel were then analyzed in the same way in accordance with the boiling point distribution determination by gas chromatography given in ASTM D-2287-73.

The analyses were carried out on a Hewlett Packard Model 7620A Gas Chromatograph with a flame ionization detector. The columnn was 1/8" O.D. x 6' stainless steel column packed with OV 101 (methyl silicone) on Chromosorb W-HP (flux calcined diatomite) which was temperature programmed at 6°C/min. from 0°C to 350°C. The 0.5 ml samples were further concentrated to 25 ul before injection and one microliter of sample was injected in all cases.

For calibration purposes several known paraffins were chromatographed under the same conditions as the samples. Results in Table 68 show the relationship between boiling point of the paraffin and column temperature at which elution occurred.

TABLE 64. BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - Low Sulfur Fuel (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
02 20	T	16 38	0.011
02 47	0.021	16 93	0.006
02 78	0.004	17 46	0.009
03 74	T	17 97	0.001
04 10	0.001	18 47	0.005
04 22	0.007	18 87	T
04 45	T	19 43	0.002
04 60	0.003	20 37	0.001
04 70	0.004	21 25	T
04 88	0.008	22 91	T
04 96	0.001	23 16	T
05 13	0.097	24 43	0.001
05 39	0.052		
05 63	0.149		
06 07	0.517		
06 30	0.197		
06 44	0.418		
06 76	0.868		
06 88	0.611		
07 24	2.198		
07 58	0.846		
07 92	4.732		
08 27	2.638		
08 42	4.141		
08 85	6.498		
09 21	4.437		
09 39	4.471		
09 78	5.854		
10 06	2.990		
10 36	8.107		
10 74	7.268		
10 98	1.858		
11 24	6.676		
11 51	2.326		
11 74	5.471		
11 92	3.856		
12 13	2.883		
12 47	3.730		
12 65	3.243		
12 97	3.407		
13 15	9.252		
13 87	0.002		
14 14	0.100		
15 27	0.020		

TABLE 65. BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - Low Sulfur Fuel (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
01 76	0.001	13 83	0.437
01 92	.004	14 09	1.308
02 16	.367	14 84	0.019
02 48	.012	15 25	0.043
02 96	.002	15 96	0.107
03 54	.002	16 37	0.041
03 84	.003	16 94	0.007
04 00	.006	17 41	0.012
04 39	.003	18 40	0.089
04 51	.003	19 08	0.005
04 79	.003	19 44	0.003
04 96	.101	20 37	0.003
05 24	.052	20 56	0.006
05 49	.180	21 24	0.002
05 96	.635	21 58	0.011
06 20	.215	21 92	0.008
06 43	.156	22 07	0.007
06 56	1.018	22 41	T
06 80	.883	22 88	0.002
07 16	3.520	23 16	T
07 48	1.326	23 66	0.002
07 74	5.457	24 42	0.005
08 19	6.712	25 16	0.001
08 39	2.952	25 98	T
08 78	8.897	27 40	T
09 13	6.988	33 88	T
09 31	3.426	34 10	T
09 70	6.627	35 93	T
09 95	3.073	36 08	T
10 29	9.342	35 09	T
10 49	2.226		
10 64	4.656		
11 04	2.983		
11 13	3.200		
11 40	2.441		
11 65	5.648		
11 83	3.127		
12 00	2.145		
12 30	1.640		
12 40	0.847		
12 56	2.327		
12 89	2.461		
13 08	0.899		
13 31	0.533		
13 52	0.778		

TABLE 66. BOILING POINT DISTRIBUTION ANALYSIS SAMPLE - High Sulfur Fuel (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
00 45	T	13 14	3.747
00 85	0.005	13 90	0.918
01 07	0.010	14 17	1.686
01 84	0.023	14 90	0.316
02 02	0.012	15 31	0.284
02 29	0.028	15 83	0.090
02 59	0.011	16 41	0.063
02 74	0.003	16 95	0.027
03 05	0.013	17 47	0.023
03 34	0.011	17 96	0.011
03 48	0.148	18 46	0.012
03 89	0.019	19 41	0.001
04 08	0.029	24 39	T
04 32	0.002	32 53	T
04 46	0.009		
04 59	0.006		
04 74	0.022		
05 03	0.151		
05 31	0.080		
05 56	0.213		
06 02	0.776		
06 26	0.308		
06 40	0.629		
06 73	1.175		
06 87	0.848		
07 24	2.833		
07 57	1.020		
07 92	5.686		
08 45	7.273		
08 87	7.041		
09 22	4.693		
09 40	4.640		
09 78	5.740		
10 05	3.108		
10 36	9.433		
10 73	6.237		
10 97	1.790		
11 22	6.081		
11 50	2.286		
11 73	4.988		
11 91	4.123		
12 13	2.010		
12 47	3.251		
12 65	2.874		
12 97	3.181		

TABLE 67. BOILING POINT DISTRIBUTION ANALYSIS SAMPLE - High Sulfur Fuel (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
00 94	T	12 59	1.804
01 97	0.001	12 92	1.877
02 07	0.006	13 09	0.633
02 24	0.011	13 34	0.416
02 51	0.743	13 56	0.349
02 86	0.019	13 64	0.236
03 39	0.003	13 86	0.372
03 71	0.006	14 12	0.763
03 84	0.013	14 56	0.042
04 28	0.015	14 70	0.065
04 44	0.021	14 86	0.233
04 65	0.001	15 26	0.241
04 78	0.008	15 80	0.105
04 89	0.007	16 36	0.101
05 16	0.006	16 92	0.035
05 30	0.157	17 44	0.018
05 56	0.079	18 45	0.014
05 77	0.257	19 45	0.002
06 20	0.958	19 86	T
06 41	0.352	20 40	0.002
06 62	0.238	20 56	0.002
06 84	1.379	21 27	0.001
06 98	1.189	22 10	0.001
07 33	4.488	22 93	0.001
07 65	1.629	23 70	0.001
07 93	6.226	34 07	T
08 18	1.257	37 08	T
08 35	5.433	34 14	T
08 55	3.246	37 40	0.004
08 92	9.037	37 44	0.004
09 25	7.125		
09 43	3.905		
09 80	6.184		
10 04	3.197		
10 36	8.981		
10 56	2.282		
10 70	4.617		
11 10	2.777		
11 19	2,859		
11 46	2.352		
11 69	4.969		
11 87	2.740		
12 04	1.980		
12 32	1.286		
12 44	0,635		

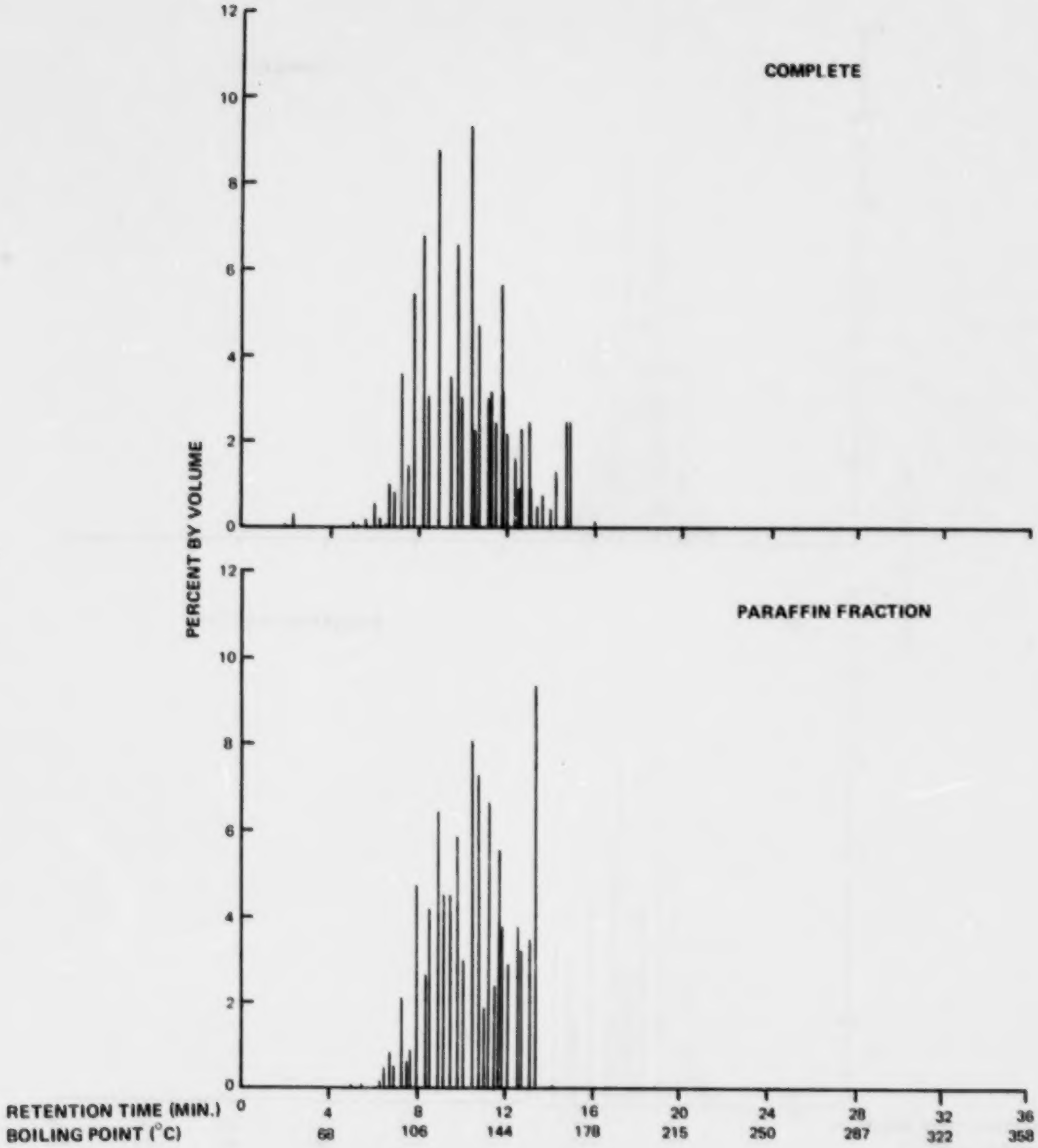


Figure 53. Graphic representation of boiling point distribution for tables 64 and 65.

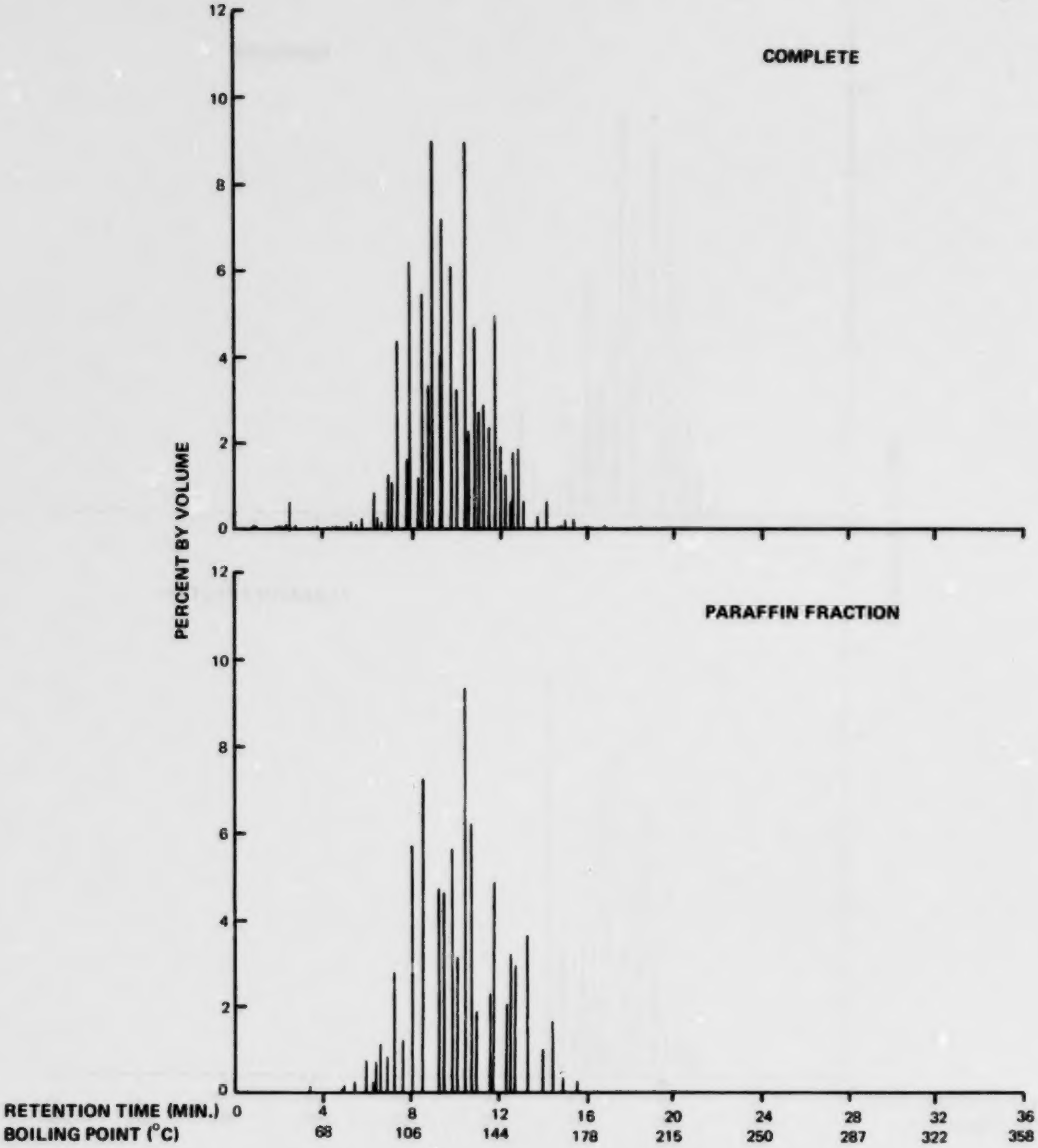


Figure 54. Graphic representation of boiling point distribution for tables 66 and 67, high sulfur fuel.

TABLE 68. B.P. OF KNOWN PARAFFINS AND COLUMN TEMPERATURE AT ELUTION

Compound	Boiling Point °C	Column Temperature at Elution, °C
Hexane	68	24
Octadecane	304	184
Eicosane	343	203

Table 68 gives the elution times which correspond to degrees Celsius at which the component is eluted and the relative abundance in percentages. Table 69 (a thru p) also shows the total response for the sample. These abundances are shown graphically for samples collected at idle and takeoff power points only using both high and low sulfur fuels (Figures 55 through 58).

In all cases, hexane is excluded. The bulk of the components of the paraffin samples eluted at column temperatures between 140 and 280°C. For samples from which the paraffins were not removed, the range was 100 to 300°C.

The fuel components eluted between 60°C to 140°C for both the total sample and the paraffin portion. (See Tables 52 through 55.) This fuel was found on analysis by the ASTM D-1319-70 method to be 19.6% aromatics and 0.3% olefins with the balance paraffins. Such a breakdown of the samples was not possible because of the small amount of aromatic and olefins present compared with the large amount of hexane, a paraffin, used as a solvent.

Sulfur Oxides Emissions

A determination of sulfur oxides emissions was made in two tests using low sulfur Jet A-1 fuel (ASTM D-1655-75) and Jet A-1 doped to an approximate 0.25% sulfur concentration with ditertiary butyl disulfide. The engine was run at four power settings using low sulfur fuel (idle, approach, climb, takeoff) and three power settings using the doped high sulfur fuel (idle, approach, climb). Takeoff power was unattainable during the high sulfur fuel tests due to engine temperature limitations brought about by an unusually high ambient temperature level.

Sulfur oxides were collected from the exhaust stream using the high volume linear sampling rake and mixing plenum. A 1/4" O.D. stainless steel emissions line delivered samples from the plenum to the sulfur oxides absorption train. The line was heated to 150°C.

TABLE 69 (a). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 1A (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
04 01	0.111	23 46	0.578
04 15	0.070	23 92	0.305
05 11	0.108	24 20	2.097
05 24	1.419	24 66	1.248
05 61	0.657	24 92	0.817
05 95	0.531	25 15	0.038
07 74	0.126	25 52	0.479
07 96	0.121	26 16	2.702
08 56	0.039	26 50	0.326
10 43	0.026	26 78	0.163
11 61	0.053	27 42	1.078
11 69	0.030	28 03	1.821
11 84	0.115	28 63	0.162
12 01	0.247	29 20	0.746
12 23	0.971	29 73	1.649
12 37	0.547	30 02	0.123
12 58	0.284	30 31	0.201
12 77	0.707	30 94	0.967
13 04	2.476	31 32	1.534
13 26	1.892	31 96	0.680
13 51	1.119	32 90	0.239
13 82	2.414	33 18	0.032
14 02	1.544	33 40	0.061
14 61	8.147	33 62	0.151
14 81	1.513	34 04	0.254
15 17	2.128	34 84	0.001
15 46	0.542	36 18	0.036
15 98	5.855	36 52	0.001
16 39	0.028		
16 55	0.260		
16 82	0.044		
17 06	0.107		
17 30	0.385		
17 51	0.719		
18 29	0.213		
18 50	0.256		
19 37	39.587		
20 10	0.562		
20 50	0.604		
21 10	0.363		
21 36	0.289		
21 55	0.065		
21 98	1.429		
22 30	1.437		
22 74	0.722		
23 22	0.649		

TABLE 69 (b). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 1A (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
04 28	0.107	23 35	2.103
04 61	0.094	23 58	5.681
05 31	0.093	23 90	3.076
05 89	0.011	24 10	1.933
06 21	0.015	24 33	5.369
06 86	0.007	24 64	2.418
07 98	0.004	24 79	2.193
08 29	0.105	25 05	4.860
08 73	0.014	25 34	2.792
08 84	0.090	25 49	1.536
08 94	0.012	25 75	3.781
09 18	0.085	26 00	2.302
09 75	0.059	26 42	4.079
10 27	0.176	26 64	4.112
10 51	0.008	27 07	2.438
11 16	0.086	27 27	2.892
11 64	0.170	27 70	3.969
11 93	0.048	28 30	3.717
12 45	0.069	28 90	3.027
02 58	0.017	29 49	1.159
12 93	0.151	29 69	0.887
13 70	0.064	30 06	1.290
13 87	0.036	30 62	0.433
14 14	0.187	34 78	3.3
14 88	0.165	34 78	0.036
15 28	0.263		
15 86	0.103		
15 95	0.069		
16 37	0.286		
16 91	0.234		
17 04	0.082		
17 42	0.590		
17 94	0.265		
18 42	0.730		
18 97	0.755		
19 37	1.189		
19 92	0.957		
20 28	1.829		
21 16	4.532		
21 78	3.945		
22 00	3.856		
22 37	2.372		
22 56	2.036		
22 90	5.563		
23 16	2.356		

TABLE 69 (c). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 2A (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
ION TIME	0/0	26 43	36.990
04 18	0.035	26 96	1.268
10 99	0.125	27 55	1.157
11 61	0.008	28 12	5.869
11 90	0.009	28 46	0.718
12 47	0.034	28 71	0.873
12 60	0.010	29 27	0.792
13 48	0.033	29 74	6.989
13 73	0.012	30 33	0.689
14 01	0.004	30 86	0.343
14 42	0.013	31 26	1.833
14 65	0.045	33 24	T
14 74	0.047	34 04	0.015
15 05	0.073	36 40	T
15 33	0.032		
15 83	0.001		
16 45	0.047		
16 75	0.325		
16 96	0.079		
17 31	0.007		
17 53	0.091		
17 93	0.025		
18 53	0.177		
18 75	0.263		
19 18	0.184		
19 57	18.682		
19 98	0.035		
20 39	0.165		
20 61	0.057		
20 81	0.028		
21 31	0.728		
31 65	0.472		
22 23	3.809		
22 57	0.447		
22 81	0.373		
22 99	2.490		
23 21	0.265		
23 53	1.525		
23 78	3.452		
24 29	0.577		
24 53	3.571		
24 99	1.155		
25 27	1.542		
25 74	0.905		
25 97	0.506		

TABLE 69 (d). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 2A (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
04 14	0.070	23 46	2.596
08 56	0.010	23 73	8.084
08 78	0.020	24 07	1.448
09 52	0.002	24 51	12.215
09 59	0.008	24 79	0.184
10 25	0.081	25 25	4.583
10 62	0.003	25 54	2.970
11 15	0.095	25 97	3.892
11 53	0.108	26 21	2.525
11 83	0.029	26 53	3.002
12 02	0.004	27 55	1.035
12 46	0.158	32 96	0.008
12 58	0.041	34 39	0.001
12 73	0.015		
12 93	0.209		
13 73	0.159		
13 90	0.086		
14 16	0.229		
14 77	0.037		
14 92	0.113		
15 32	0.297		
15 86	0.174		
16 05	0.178		
16 42	3.177		
16 73	0.080		
16 96	0.653		
17 11	0.252		
17 49	1.612		
17 75	0.323		
18 01	1.156		
18 16	0.736		
18 47	2.151		
19 03	2.330		
19 43	2.582		
20 35	3.240		
21 23	2.289		
21 45	4.870		
21 88	5.865		
22 07	5.332		
22 45	3.746		
22 56	1.818		
22 92	8.482		
23 20	4.653		

TABLE 69 (e). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 3A (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
05 39	0.105	28 72	2.621
05 47	0.151	29 30	2.463
05 60	0.085	29 80	16.623
06 65	0.001	30 40	2.059
14 72	1.089	30 94	2.133
15 09	0.271	31 38	4.598
15 32	0.196	31 96	2.117
15 79	0.084	32 50	0.970
16 40	0.316	32 98	1.880
16 70	0.613	33 42	1.444
16 91	0.281	33 74	0.959
17 08	0.447	34 18	1.333
17 28	0.126		
17 50	0.419		
18 01	0.091		
18 52	0.669		
18 77	0.596		
19 07	0.190		
19 21	0.365		
19 51	1.024		
19 61	1.146		
20 44	1.221		
20 86	0.105		
21 32	2.445		
21 66	0.810		
22 20	3.051		
22 30	0.981		
22 78	0.767		
23 00	0.337		
23 27	0.030		
23 52	1.088		
23 74	0.547		
23 92	0.061		
24 50	10.300		
24 96	0.638		
25 18	0.322		
25 70	1.444		
26 34	4.418		
26 64	1.496		
26 88	1.313		
27 52	2.924		
28 10	17.283		
28 46	0.958		

TABLE 69 (f). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 3A (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
04 52	0.112		
04 59	0.032		
08 17	0.089		
08 64	0.030		
12 33	0.027		
14 33	0.009		
14 79	0.003		
1521	0.195		
16 29	0.387		
16 81	0.552		
16 98	0.056		
17 35	0.712		
17 85	0.142		
18 32	1.810		
18 91	1.234		
19 26	2.764		
20 18	2.530		
21 04	6.995		
21 88	14.609		
22 44	6.295		
22 68	0.378		
23 00	4.057		
23 46	5.530		
23 78	4.925		
24 20	7.759		
24 52	3.953		
24 92	6.434		
25 62	6.168		
26 28	9.380		
26 94	5.501		
27 56	3.593		
28 16	2.521		
28 80	0.915		
29 42	0.425		
30 66	0.009		
31 24	0.018		
33 38	0.012		
34 28	0.003		

TABLE 69 (g). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 4A (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
04 10	0.065	28 08	13.947
04 23	0.045	28 41	0.560
11 89	0.002	28 68	1.874
13 66	0.021	29 24	2.872
14 67	0.893	29 74	11.206
14 97	0.072	30 32	1.194
15 05	0.043	30 86	1.278
15 29	0.051	31 30	2.906
15 80	0.076	31 88	0.879
16 19	0.152	32 44	0.276
16 41	0.333	32 78	0.888
16 71	0.596	33 28	0.520
16 93	0.278	33 64	0.212
17 09	0.595	34 08	0.723
17 30	0.239	34 52	0.001
17 52	0.459		
17 57	0.170		
17 73	0.975		
17 98	0.448		
18 21	0.461		
18 51	0.871		
18 70	2.274		
19 03	1.242		
16 58	2.611		
19 96	0.511		
20 16	0.985		
20 40	1.315		
20 60	0.687		
20 80	0.675		
20 93	0.842		
21 32	1.527		
21 62	0.245		
22 06	0.996		
22 28	2.685		
22 74	0.518		
23 60	3.321		
24 46	10.959		
24 90	0.615		
25 16	0.108		
25 60	5.131		
26 30	8.319		
26 62	0.706		
26 86	1.062		
27 22	0.075		
27 48	6.403		

TABLE 69 (h). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 4A (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
04 77	0.100	30 80	1.142
05 44	1.257	32 36	0.135
06 36	0.156	33 30	0.010
06 98	0.100	35 46	0.322
07 49	0.210	36 91	0.042
08 74	0.249	37 12	0.145
08 87	0.197		
09 20	0.395		
09 78	0.447		
09 95	0.031		
10 34	0.758		
11 22	0.862		
11 70	0.457		
12 47	0.363		
13 01	0.457		
13 35	0.582		
13 85	0.114		
16 07	0.210		
16 45	1.340		
16 70	0.145		
16 98	3.323		
17 51	2.409		
18 32	0.509		
18 52	3.001		
19 07	3.863		
19 49	3.998		
20 18	1.392		
20 42	1.516		
20 98	7.363		
22 16	6.034		
22 98	6.699		
24 08	3.988		
25 24	8.952		
26 18	12.670		
27 49	9.970		
28 85	2.119		
29 10	4.912		
19 68	3.396		
29 95	1.423		
30 28	2.804		

TABLE 69 (i). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 1B (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
10 87	0.035		
14 65	0.207		
15 94	0.069		
16 40	5.392		
17 00	0.207		
17 32	3.180		
17 57	0.104		
17 77	1.348		
18 10	0.069		
18 55	2.904		
19 17	1.106		
19 63	18.977		
20 19	0.518		
20 43	1.797		
20 67	1.521		
21 35	0.933		
21 57	3.422		
22 27	7.397		
23 05	1.659		
23 27	0.760		
23 53	19.564		
24 51	8.434		
24 80	0.933		
25 05	2.627		
25 23	4.770		
25 47	0.622		
26 41	3.802		
28 41	1.521		
28 73	0.346		
29 35	2.523		
32 91	1.936		
33 39	1.279		
34 17	0.035		

TABLE 69 (j). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 1B (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
07 29	0.004	26 91	3.096
10 23	0.087	27 26	5.425
10 48	0.020	27 88	5.023
10 57	0.045	28 46	3.789
11 12	0.167	29 10	2.965
11 37	0.006	29 66	1.605
11 44	0.004	30 26	1.356
11 60	0.169	30 82	0.481
11 78	0.042	31 34	0.326
12 41	0.261	31 84	0.149
12 98	0.149	32 36	0.018
13 59	0.128	34 28	0.001
13 86	0.058	36 88	0.018
14 15	0.510	37 22	0.008
14 92	0.193		
15 33	0.291		
16 45	0.428		
16 99	0.570		
17 51	0.972		
18 03	0.748		
18 51	1.408		
19 46	0.756		
20 02	0.498		
20 38	1.538		
20 96	1.483		
21 26	1.968		
21 48	3.976		
22 12	4.398		
22 68	3.640		
22 92	5.963		
23 28	1.277		
23 46	2.116		
23 72	5.664		
24 04	2.435		
24 22	1.439		
24 46	5.665		
24 78	1.979		
24 94	1.775		
25 20	4.298		
25 50	4.074		
25 90	3.299		
26 18	3.993		
26 60	4.928		

TABLE 69 (k). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 2B (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
04 02	0.424		
04 16	0.442		
13 77	0.617		
14 73	0.085		
15 00	1.029		
15 32	0.006		
15 79	1.090		
16 42	0.224		
16 72	0.569		
16 91	0.018		
17 35	0.206		
18 52	0.841		
18 83	0.436		
19 22	1.120		
19 60	61.168		
20 44	0.454		
20 62	0.278		
21 30	0.593		
21 64	0.884		
22 28	6.562		
22 80	1.144		
22 96	1.168		
23 20	1.816		
23 50	1.913		
23 78	1.059		
24 48	7.161		
24 92	0.484		
25 22	0.091		
26 42	2.264		
26 66	0.006		
27 54	0.012		
27 96	0.430		
28 22	1.047		
29 28	0.460		
29 94	1.701		
30 38	1.289		
32 54	0.266		
33 58	0.073		
33 98	0.248		
34 36	0.006		
34 50	0.006		
35 12	0.012		
36 78	0.224		
37 06	0.067		

TABLE 69 (I). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 2B (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
09 57	0.006		
14 11	0.104		
14 93	0.043		
15 25	0.448		
15 83	0.021		
16 32	1.400		
16 87	0.457		
17 02	0.110		
17 91	0.274		
18 40	2.062		
19 03	0.962		
19 39	1.486		
20 32	0.618		
20 51	0.402		
21 20	3.572		
22 05	12.711		
22 61	4.492		
22 87	7.464		
23 20	3.944		
23 41	2.183		
23 65	7.458		
23 99	3.453		
24 18	3.201		
24 40	10.250		
24 72	0.850		
24 85	7.552		
25 14	8.006		
25 43	5.016		
25 83	6.885		
26 10	1.270		
26 51	0.691		
27 83	1.880		
28 40	0.292		
31 38	0.012		
36 15	0.012		
37 03	0.015		

TABLE 69 (m). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 3B (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
07 66	0.003	26 82	2.537
07 75	0.001	27 44	0.586
08 81	0.002	24 86	1.517
12 49	0.225	28 40	2.617
12 96	0.001	31 90	0.008
13 51	0.002	34 65	T
13 80	0.019		
14 80	0.001		
15 06	0.019		
15 54	0.012		
15 96	0.016		
16 17	0.001		
16 24	0.002		
16 45	0.022		
16 77	0.011		
17 07	0.041		
17 53	0.029		
18 52	0.049		
18 80	0.025		
19 18	0.226		
19 70	73.353		
20 38	0.670		
20 58	0.480		
20 94	0.498		
21 28	0.676		
21 58	0.646		
22 18	1.350		
22 48	0.644		
22 70	0.453		
22 92	0.842		
23 18	0.547		
23 44	0.745		
23 70	0.730		
23 90	1.059		
24 42	2.292		
24 92	1.180		
25 16	1.162		
25 66	1.469		
25 86	0.894		
26 40	1.700		
26 58	0.637		

TABLE 69 (n). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 3B (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
03 98	0.049		
04 11	0.130		
05 11	0.347		
11 73	0.081		
13 03	0.046		
13 91	0.011		
15 39	0.103		
16 47	0.678		
17 01	0.079		
17 52	0.613		
18 22	0.003		
18 51	1.120		
19 13	0.908		
19 47	0.504		
19 59	3.752		
20 38	0.160		
21 25	0.984		
22 08	3.300		
22 46	3.324		
22 89	3.446		
23 68	1.754		
24 43	78.486		
29 65	0.011		
30 80	0.111		

TABLE 69 (o). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 4B (Complete)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
13 53	0.042	32 05	0.420
14 53	0.021	32 38	0.558
14 63	0.032	32 76	0.698
14 86	0.045	32 92	0.597
16 27	0.009	33 58	0.083
16 57	0.037	34 46	0.001
17 11	0.054	36 28	0.006
17 33	0.129	36 54	0.003
17 59	0.101	37 00	0.005
17 88	0.004		
18 33	0.097		
18 57	0.036		
18 96	0.292		
19 38	64.858		
20 16	0.046		
20 60	0.005		
20 92	0.016		
21 06	0.179		
21 42	0.081		
22 00	0.951		
22 42	0.180		
22 86	1.196		
23 14	0.122		
23 42	1.214		
23 68	1.243		
24 46	3.889		
24 94	0.361		
25 20	0.566		
25 50	0.357		
25 78	1.217		
26 34	4.032		
26 88	0.194		
27 14	0.330		
27 52	1.200		
28 10	2.741		
28 68	0.615		
29 24	1.505		
29 74	4.307		
30 30	0.841		
30 86	1.119		
31 26	2.702		
31 86	0.663		

TABLE 69 (p). BOILING POINT DISTRIBUTION ANALYSIS
SAMPLE - BP - 4B (Paraffin Fraction)

Retention Time, Minutes	Percent By Volume	Retention Time, Minutes	Percent By Volume
16 40	3.228		
18 50	7.215		
19 10	3.101		
19 50	1.392		
20 56	6.266		
21 08	0.316		
21 30	2.089		
22 10	17.025		
22 66	1.392		
22 92	6.139		
23 20	1.456		
23 70	3.987		
24 46	7.405		
25 18	2.722		
25 44	0.696		
25 86	1.392		
31 76	0.696		
32 86	2.595		
33 04	3.038		
33 34	18.101		
33 78	6.392		
34 06	3.291		
34 58	0.063		

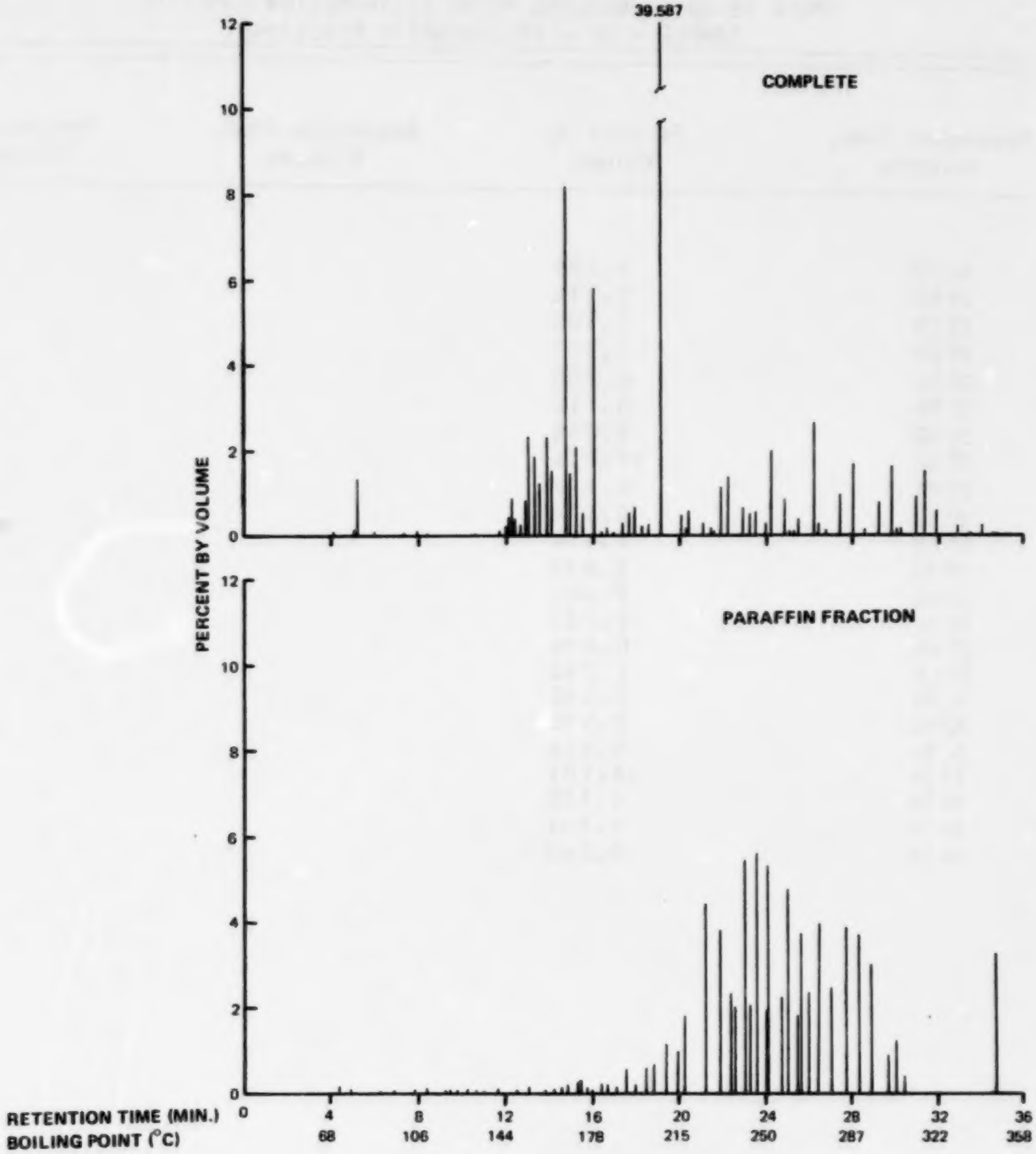


Figure 55. Graphic representation of boiling point distribution for tables 69 (a and b). idle power point (1A) using low sulfur fuel.

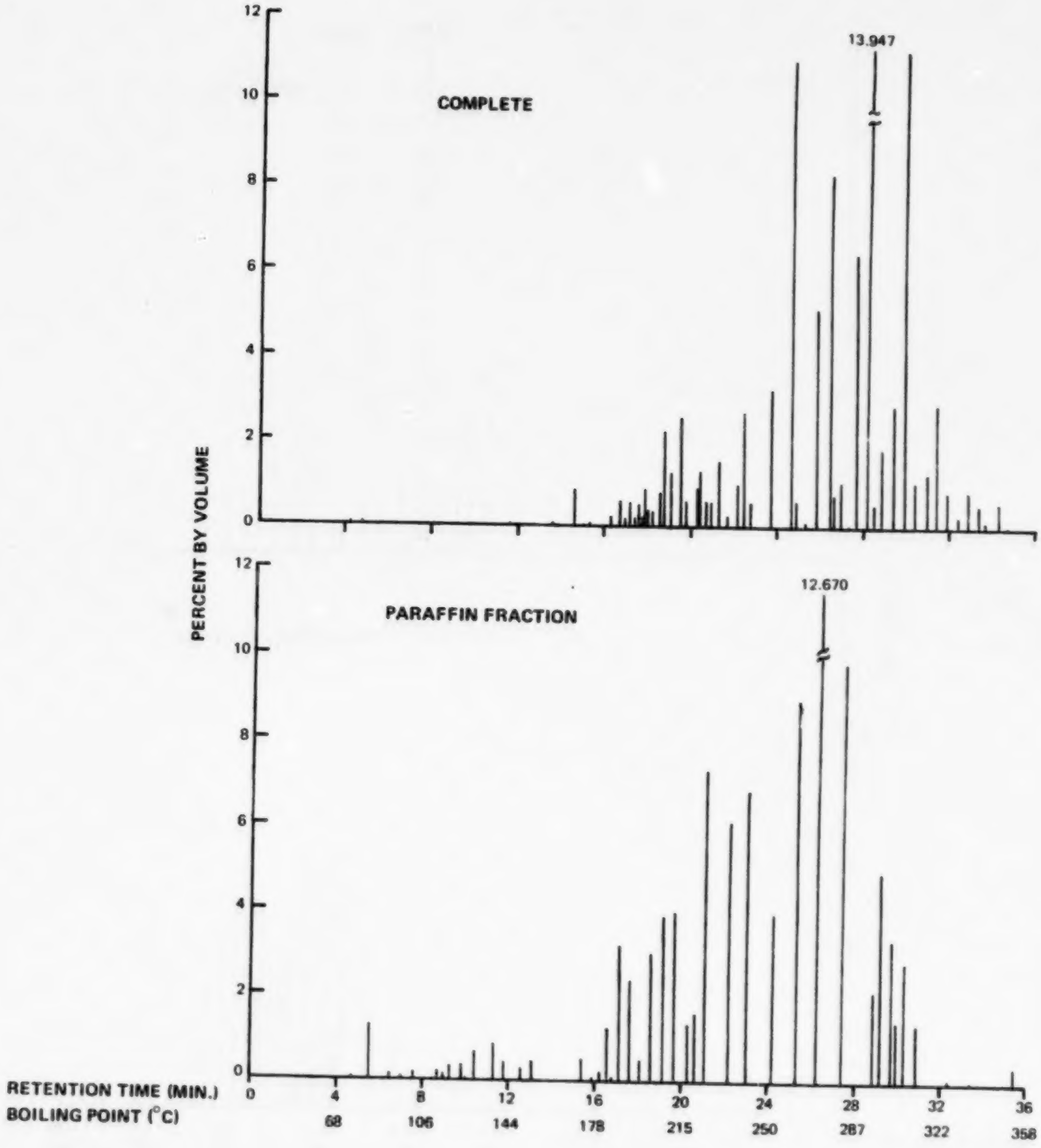


Figure 56. Graphic representation of boiling point distribution for tables 69 (g and h) takeoff power point (4A) using low sulfur fuel.

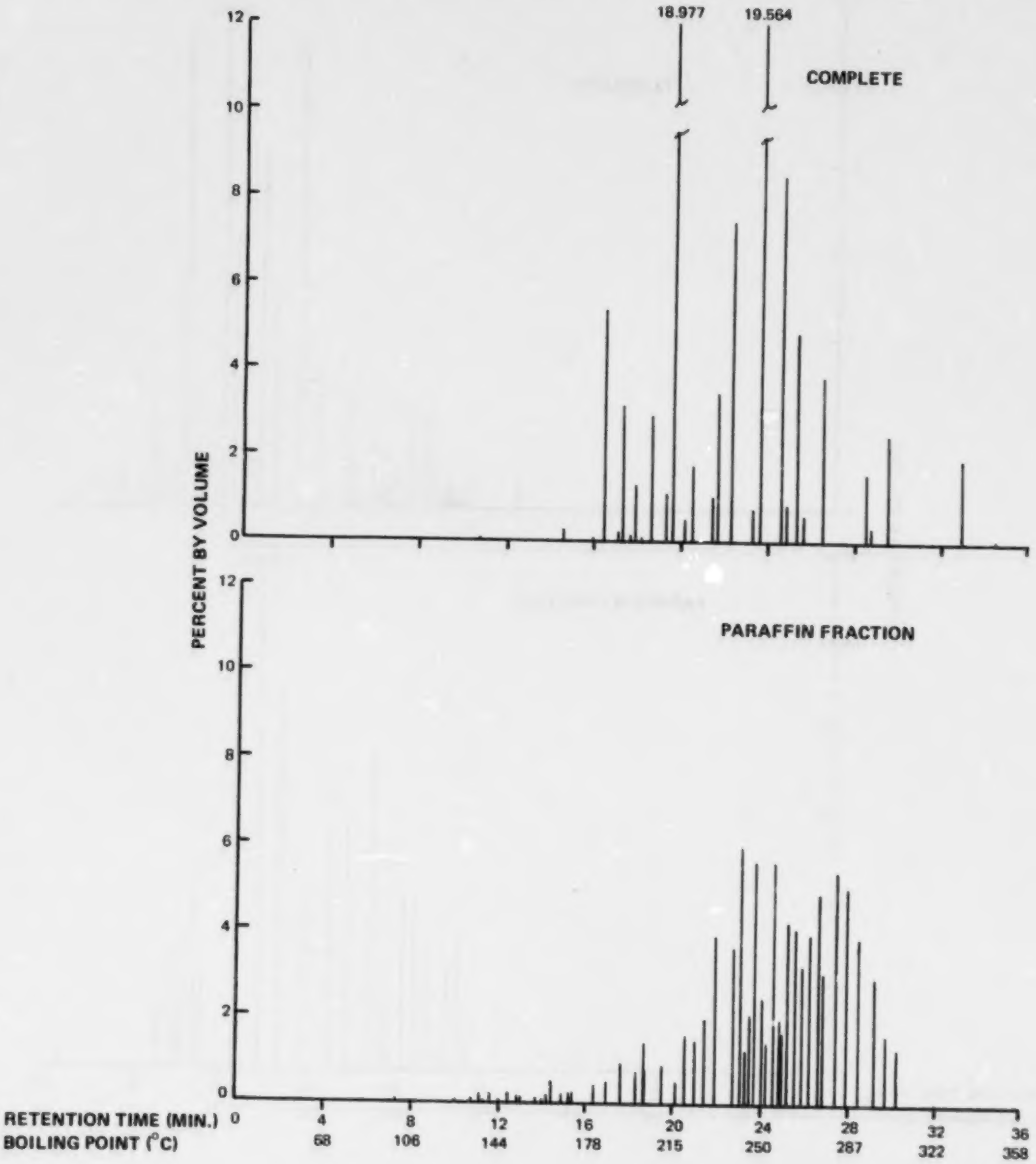


Figure 57. Graphic representation of boiling point distribution for tables 69 (i and j) idle power point (1B) using high sulfur fuel.

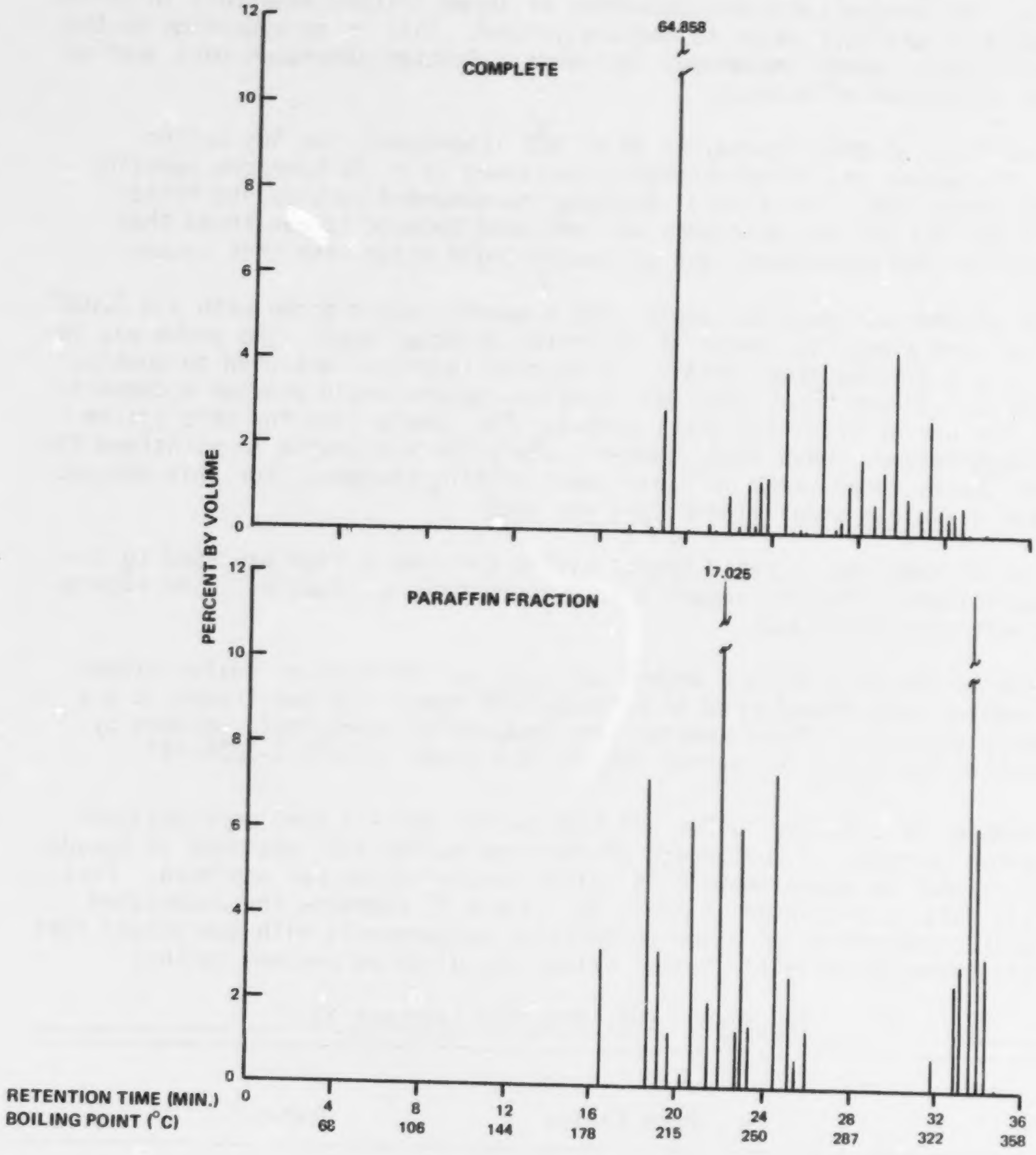


Figure 58. Graphic representation of boiling point distribution for tables 69 (o and p) takeoff power point (4B) using high sulfur fuel.

The absorption train used was similar to that described in method 8 of the Federal Register, "Standards of Performance for Stationary Sources", June 8, 1976. The absorption train consisted of three fritted absorbers in series followed by a dry test meter to measure volume. This is an exception to the Federal Register which recommends impingers. Fritted absorbers were used to improve collection efficiency.

The first absorber contained 15 ml 80% isopropanol for SO_3 collection. The second and third absorbers contained 15 ml 3% hydrogen peroxide each to absorb SO_2. The Federal Register recommended particulate filter between the SO_3 and SO_2 absorbers was not used because it was found that condensation and subsequent loss of sample could occur with this system.

An attempt was made to sample with a quartz sample probe with six 0.030" holes drilled along its length at centroids of equal area. The probe was encased in a stainless steel sheath. A ceramic separator was used to cushion the quartz. It was hoped that this sampling scheme would provide a comparison to the use of stainless steel probes. The sample line for this system was heated teflon. When used, however, the probe was unable to withstand the thermal shocks encountered in rapid power setting changes. For this reason, only the stainless steel linear rake was used.

In all sampling, a rapid bypass system for sample flow was used to decrease residence time and insure a more representative sample. Line adsorptions were thus minimized.

The barium chloranilate method was used for analysis of sulfur oxides. Test samples were transferred to polyethylene containers and frozen in dry ice until analysis. These samples were reduced to approximate volumes by evaporative heating. The method details are given in ASTM D-3226-73T.

Samples of both low sulfur and high sulfur Jet A-1 fuel were analyzed for sulfur content. A spot check of the high sulfur fuel was made in Canada to assure that an approximate 0.3% sulfur concentration was achieved. Fuel analysis data is presented in Table 70. Table 71 compares the calculated fuel sulfur concentration based on emission measurements with the actual fuel analysis shown in Table 71. Sulfur oxides are given as percent sulfur.

TABLE 70. FUEL ANALYSIS (percent S)

Sample	P&WA Canada	P&WA-U.S.
Low Sulfur		0.006 0.007
High Sulfur	0.2500	0.2600 0.2500

TABLE 71. PERCENT SULFUR IN FUEL BASED ON EMISSION MEASUREMENTS

Power Setting	% Sulfur in Fuel Based on SO_2 Emission	% Sulfur in Fuel Based on SO_3 Emission	Total % Sulfur in Fuel Based Emission
Jet A-1 Low Sulfur Fuel			
Idle	No SO_2 detected	No SO_3 detected	No SO_x detected
Approach	No SO_2 detected	No SO_3 detected	No SO_x detected
Climb	0.0035	No SO_3 detected	0.0035
Take-Off	0.0179	No SO_3 detected	0.0179
Jet A-1 High Sulfur Fuel			
Idle	0.2279	0.0104	0.2383
Approach	0.2769	No SO_x detected	0.2769
Climb	0.2638	0.0294	0.2932

A good material balance was achieved between fuel bound sulfur and exhaust samples at all power settings. On an average, a relative error of 6% exists between the fuel sulfur concentration determined in the analysis of the high sulfur fuel and the fuel sulfur concentration calculated from measured gaseous SO_x emissions. The overall limitations of the sampling method are obvious in the low sulfur runs where adsorption losses can easily account for the absence of sulfur at low power. The high sulfur sample runs do not suffer this limitation and essentially all the sulfur expected was detected.

Proton Activation Analysis/X-Ray Analysis

Nuclepore filters were used to collect particulates while the engine was operated at four power settings using high and low sulfur fuels. Repeat samples were taken at four power settings using low sulfur fuel making a total of twelve exposed filters.

These twelve Nuclepore filters were submitted to the EPA for proton activation analysis (PAA) which was carried out at the Florida State University (FSU) Physics Department. This type of analysis resulted in an elemental assay of the particulates adhering to the filter material. Results of this analysis are shown in Table 72. The data from FSU is reported on the basis of concentration with respect to unit area. The data supplied by FSU was further reduced to reconcile the concentration of the various elements with respect to exhaust gas flow, and is given in Table 73. A clean Nuclepore filter was analyzed by PAA as a blank and the resulting data was subtracted from the particulate data before the data was reduced as described above.

Mitex filters were used to collect particulate material while the engine was operating at four power settings and using high and low sulfur fuel. One repeat sample was taken at the take-off power condition using low sulfur fuel to give a total of nine particulate laden filters. These nine filters were sent to the EPA at Research Triangle Park where the surfaces were analyzed using X-ray techniques. The data, reported in concentrations per unit area, was reduced to reflect concentrations in terms of nanograms of each element per m^3 flow. These results are given in Table 74.

TABLE 72. PROTON ACTIVATION ANALYSIS DATA FROM FSU REPORT

Run #	Al	Si	P	S	Cl	K	Ca	Cr	Fe	Ni	Cu	Zn	Br	Pb
Climb 64	-	274	80	389	353	38	58	172	453	397	56	83	16	37
Climb 72	60	221	56	369	428	10	75	88	437	152	34	83	16	39
Approach 67	33	240	99	271	269	-	16	39	184	94	17	39	14	10
Approach 80	-	235	61	244	195	-	-	25	48	35	10	9	33	25
Take-off 70	-	339	80	400	487	24	61	125	309	210	39	38	23	32
Take-off 83	-	305	119	493	521	-	29	159	449	330	49	65	24	34
Idle 74	-	201	34	158	162	14	27	4	51	29	9	12	15	16
Idle 78	96	303	89	208^3	184	-	9	-	18	15	8	-	23	14
Approach 84 High-Sulfur	-	309	90	1144	436	12	51	150	921	306	52	82	112	57
Take-off 85 High Sulfur	-	341	108	1645^3	867	28	57	349	1178	803	86	109	35	56
Climb 86 High Sulfur	89	555	173	1092^3	351	49	86	107	327	328	30	65	40	37
Idle 87 High Sulfur	64	330	52	483	196	27	36	58	153	115	15	25	27	16
Blank	127	212	76	137	91	-	-	7	8	7	6	-	5	10
Detection Limits	77	49	41	31	30	25	21	11	6	5	5	4	2	12

NOTE:

1. All amounts are in ng/cm^2.
2. Blank values have not been subtracted.
3. Sulfur values checked with PESA (Proton Elastic Scattering Analysis).

TABLE 73. PROTON ACTIVATION ANALYSES CONCENTRATIONS, ng/m^3

Sample	Flow m^3	Al	Si	P	S	Cl	K	Ca	Cr	Fe	Ni	Cu	Zn	Br	Pb
1A	5.67	-	-	-	20	63	12	24	-	38	20	3	11	9	5
1A	6.14	-	75	11	58	77	-	7	-	8	7	2	-	15	3
2A	3.66	-	39	32	185	246	-	22	44	243	120	15	54	12	0
2A	3.15	-	37	-	172	167	-	-	29	64	45	6	14	45	24
3A	1.69	-	186	12	756	768	114	174	495	1335	1170	150	249	33	81
3A	1.73	-	26	-	680	987	29	220	237	1257	425	822	43	32	85
4A	1.59	-	405	13	839	1263	76	194	376	960	648	105	121	57	70
4A	1.42	-	352	154	1271	1535	-	104	542	1574	1153	154	222	68	86
1B	3.64	-	164	0	481	146	38	50	71	202	150	12	35	30	8
2B	2.82	-	176	25	1813	621	22	92	257	1643	538	83	148	193	85
3B	1.63	-	1067	302	2970	809	152	267	311	992	998	75	202	109	84
4B	1.64	-	399	105	4660	2398	86	176	1057	3615	2460	247	337	93	142

Exposed filter area 5.07 cm^2

TABLE 74. X-RAY ANALYSES CONCENTRATIONS, ng/m^3

Sample	Flow m^3	Al	Si	P	S	Cl	K	Ca	Fe	Ni	Cu	Zn	Pb	Mn	Cd
1A	0.730	210	480	140	5700	1180	140	480	3090	-	-	710	-	-	-
2A	0.674	260	260	-	22900	2320	-	510	2230	-	-	-	-	-	230
3A	0.706	490	980	490	23840	6390	-	1230	35150	-	-	3200	-	-	4420
4A#1	0.659	500	750	250	25640	8710	-	500	154100	1990	-	6470	-	1000	3240
4A#2	0.697	520	1050	260	52400	6840	-	2900	16060	1320	-	1050	-	2630	2900
1B	0.760	680	-	3420	442900	-	-	460	14150	-	-	3880	-	-	180
2B	1.41	100	120	8980	344100	490	-	370	860	-	-	250	-	1350	-
3B	1.362	100	-	7130	466300	1530	-	250	21150	1270	3950	3180	5220	3690	2160
4B	0.576	900	1510	1810	228900	2100	270	900	28010	2100	-	4200	-	2710	1200

Exposed filter area 17.35 cm2

In the case of PAA, generally higher levels of all elements were found in samples from the high sulfur fuels than from samples from the low sulfur fuels at comparable engine power settings. There is some suggestion based on PAA data that engine wear increases with the high sulfur fuel. Furthermore, levels generally increased with increasing power.

The trend with X-ray analyses is less regular but many elements show a similar variation with power setting and sulfur content of fuel. The results from PAA and X-ray analysis are not directly comparable because of fundamental differences in the analytical technique and in the sampling method.

In X-ray analysis, examination of the upper surface only is involved, whereas in PAA, the total sample is analyzed. Uniformity between the sample on the surface and beneath the surface of the filter cannot be assumed. Uniformity of the collected sample cannot be assumed and may explain differences between replicate samples as well as between the PAA and X-ray analysis. Surface characteristics of Nuclepore and Mitex filters are different. Non-uniformity of the filter material would affect the uniformity of the sample. The X-ray analysis samples were taken on a large (293 mm dia.) Mitex filter and a 47 mm circle was cut and submitted for analysis. The PAA samples were taken on a pre-cut 40 mm Nuclepore filter. Differences in collection efficiency of these filter materials are probable. Possible uncertainties in sample flow measurements would also contribute to differences between X-ray and PAA data since the quantitative information is based on calculated mass accumulation from flow data. There is some suggestion based on PAA data that engine wear increases with the high sulfur fuel.

Elemental Analysis

Thirteen samples were examined for carbon, hydrogen, sulfur, oxygen, and nitrogen using traditional combustion analyzer techniques. These particulate samples were collected on 293 mm Gelman type A/E glass fiber filters using the high volume sampling system. The filter surface temperature was limited to approximately 160°F maximum and samples were taken at each of four power settings (idle, approach, climb and take-off) using both low sulfur and high sulfur fuel.

Samples were prepared for analysis by first separating the particulate matter from most of the fiber backing and desiccating the material to remove entrained water. Heat was avoided to preserve the integrity of the more volatile organic fractions. The samples were homogenized using a mixer mill and combusted in the analyzer. Table 75 lists the results of these analyses.

The data listed in Table 75 show little correlation with expected results and no correlation with power setting or fuel change. Due to the limitations of this particular analytical procedure, it is probable that insufficient material was available to accomplish a successful analysis and that a different sampling scheme would be necessary to obtain more material from the exhaust stream. Two milligrams of organic fraction would be the minimum sample required for any such sampling system design.

TABLE 75. ELEMENTAL ANALYSES

Sample	Power Setting	Total Flow, m^3	Filter Temp., °F	%C	%H	%S	%O	%N
1A #1	Idle	49.6	148	89.3	1.40	0.18	4.67	1
1A #2	Idle	20.4	142	94.0	1.41	0.04	4.54	1
2A #1	Approach	31.5	108	86.9	2.69	0.23	10.1	1
2A #2	Approach	29.4	163	95.2	1.38	1.0	3.22	1
3A #1	Climb	42.3	128	97.2	0.82	0.01	1.93	1
3A #2	Climb	42.0	116	91.6	1.92	0.18	6.33	1
4A #1	Take-off	32.2	136	95.9	1.07	0.29	2.72	1
4A #2	Take-off	43.0	144	97.5	0.65	0.26	1.56	1
4A #3	Take-off	43.7	131	96.8	0.65	0.04	2.48	1
1B	Idle	88.0	154	70.2	1.65	0.26	27.9	1
2B	Approach	42.5	150	77.5	1.70	0.32	20.5	1
3B	Climb	42.2	142	72.3	1.63	0.11	26.0	1
4B	Take-off	47.2	145	50.3	2.87	0.18	46.7	1

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APPENDIX A

GCMS ANALYSIS OF POLYNUCLEAR MIXES AND TYPICAL TURBINE COMBUSTOR EXHAUST

SAMPLES

Four samples containing polynuclear aromatic hydrocarbons were received. Three were mixes of the first sixteen compounds of Table A-1, of graded concentration, while the fourth was a representative unknown sample.

Experimental Method

The initial set of runs were performed in January, 1977. A packed, OV-1, 6 ft. glass column was used, with a temperature program of 150° to 280° at a rate of 8°/min., with a 10 minute hold at 280°. The mass spectrometer was operated in the selected mass scan mode, scanning mass ranges of 166-170, 177-180, 200-204, 226-230, 250-254, 276-280, 298-302. This technique minimizes interferences and maximizes sensitivity, and is practical when the components are known in advance. It proved quite satisfactory for the calibrating samples; Figure A-1 shows a chromatogram obtained from sample PS102, which had a concentration of 100 picograms/microliter. Table A-1 lists the peak areas found for each component in this run.

This technique proved less satisfactory for the unknown sample. It was possible to observe the anthracene/phenanthrene peaks, but little else of interest. Additionally, a large amount of silicone material was present which gave interferring peaks. An attempt was then made to fractionate and concentrate the sample. This allowed us to detect more PNAs, but the interferences from the silicone peaks were still serious. The sample was run again using chemical ionization in order to reduce the effect of the silicones. PNAs to m/e228 were detected.

When our capillary column became operational in April, the samples were rerun. This proved so superior that it was possible to run the unknown sample without concentration, or separation. Additionally, many more compounds were measured. The results of these runs are shown in Table A-1 and Figures A-2 and A-3. The column is a 20 meter, OV101 coated glass type, coupled directly to the MS without a separator. It was operated in the splitless, solvent trapping mode, with a temperature program of 30° to 180° at a rate of 16°/min., followed by a 4°/min. program to 260.

TABLE A-1

m/e	Compound	PS102[1] Packed Col.	PS102[2] Capillary	UNK #1[2] Capillary
166	Fluorene	122	139;586	110;74
178	Anthracene, Phenanthrene	1000	561;226	1000;981
202	Pyrene, Fluoranthene	306;376	405;311	88;15
228	Chrysene, Triphenylene, Benzoanthracene	826	248	19
229	Benzacridine	12;80	14	-
252	Benzo (e) pyrene, Perylene, Benzo (a) pyrene	596	54;32;53	4;2;2
276	Benzo (ghi) perylene	82;51	42;26	-
278	diBenz (a,h) anthracene	56	14	-
300	Coronene	69	-	-
		OTHER[3]		
156	Dimethyl Napthalenes	-	-	234;633; 117;50
170	Trimethyl Napthalenes	-	-	121
192	Methyl Anthracene, Methyl Phenanthrene	-	-	196;66

[1] Normalized to 1000.

[2] Capillary runs normalized to 1000, both to same scale. (Packed column to independent scale.)

[3] These components were looked for only in the unknown sample. They are representative of other polycyclics usually present as combustion products, and not exhaustive. Many others are almost certainly present.

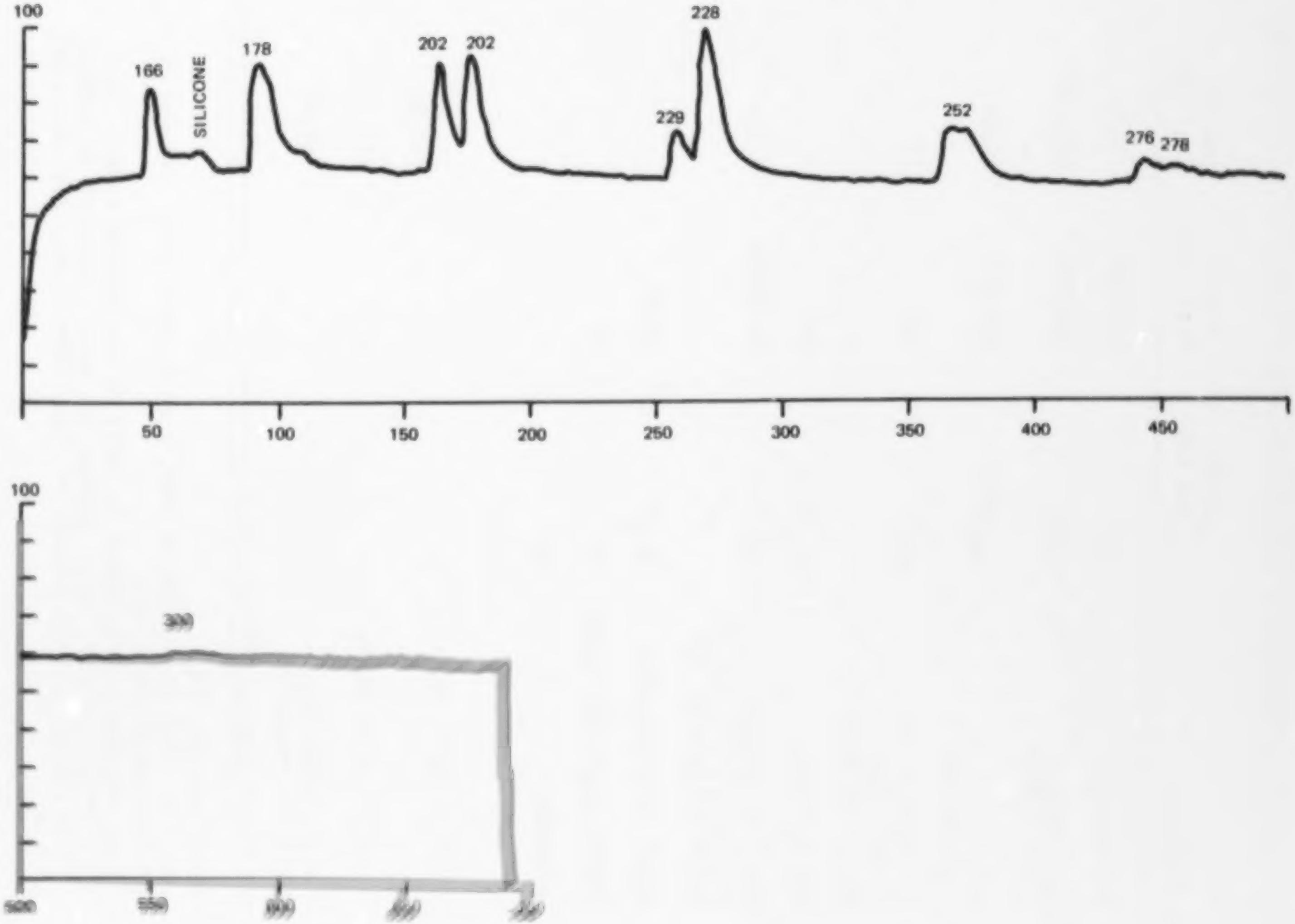

Figure A-1, Chromatogram of sample PS102 using OV-1 glass column.

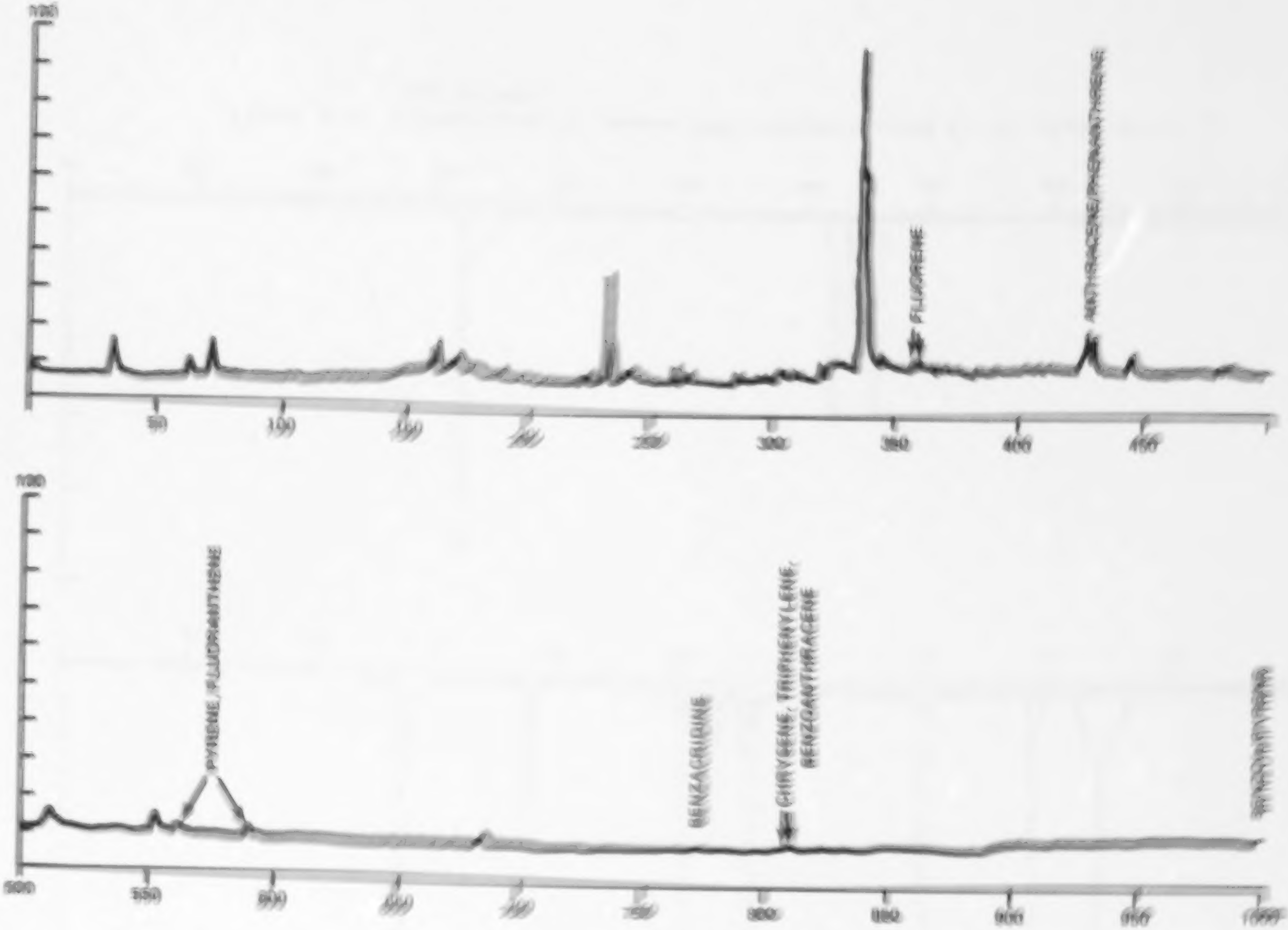

Figure A-2, Chromatogram of known PNA compounds using OV-101 glass capillary column,

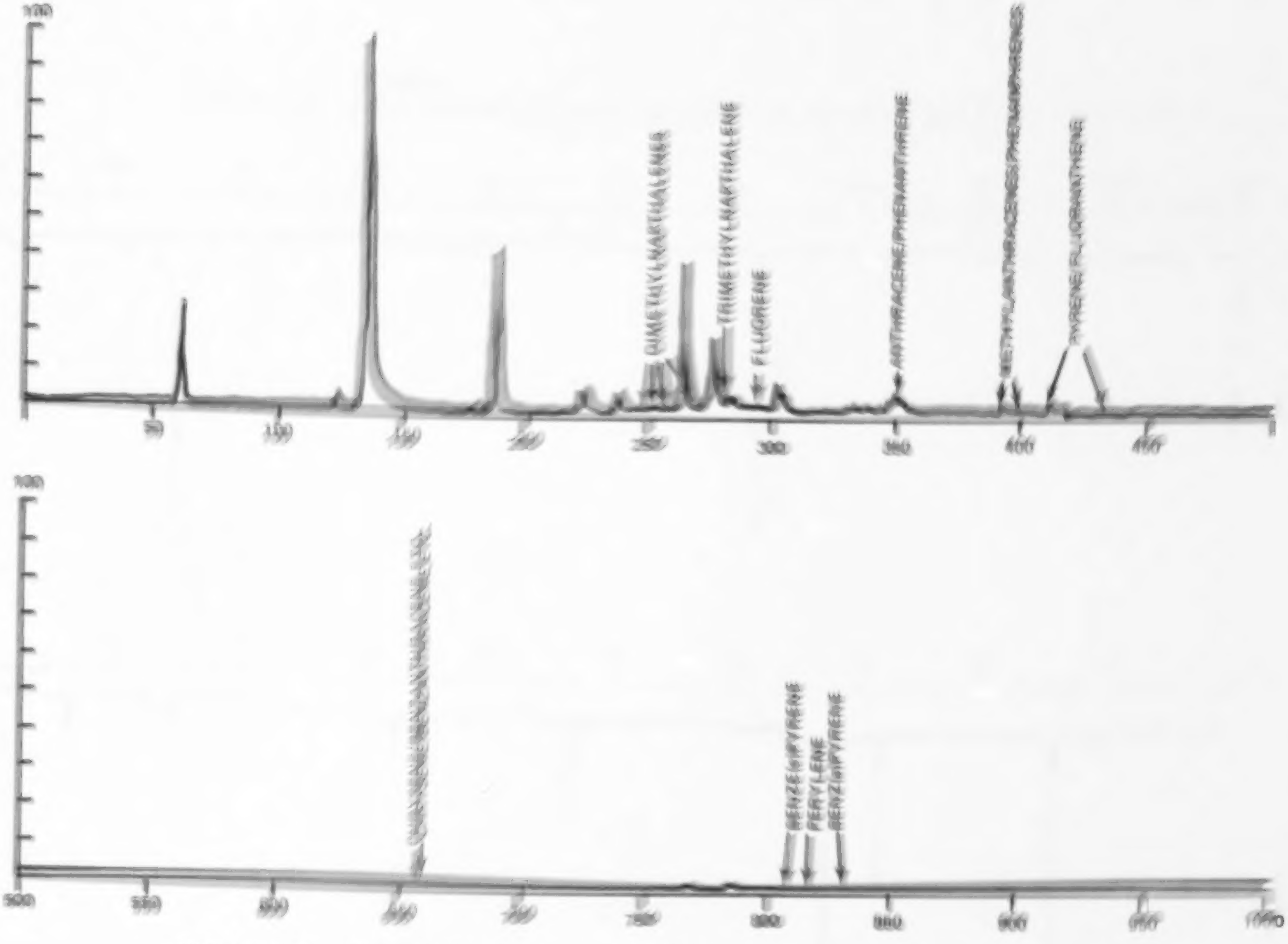

Figure A-3, Chromatogram of unknown PNA compounds using OV-101 glass capillary column.

DISCUSSION

The results listed in Table A-1 compare the data obtained on the FS102 sample with the packed and capillary columns, with a considerable time separation; and the data obtained on the FS102 and unknown #1 samples, using the capillary. The capillary runs are normalized to the same 1000 scale, and are directly comparable. Both samples were run unconcentrated, though the original value of 100 picograms/component is probably no longer valid due to the age of the sample. The large amount and number of other components can be observed in Figures A-2 and A-3. Full mass range scans were used for these runs. A sampling of alkylated PNAs were sought and found, as shown in Table A-1. Others are likely present, such as the phenyl anthracenes. It is anticipated that these will be searched for in future runs.

APPENDIX B

PNA CONTRIBUTION FROM FILTERS AND SOLVENTS*

by
D. J. Robertson, R. H. Groth, D. G. Gardner, and E. G. Glastris
Pratt & Whitney Aircraft Group
East Hartford, CT 06108

ABSTRACT

The polynuclear aromatic hydrocarbon (PNA) content of particulate matter emitted into the air from combustion or other processes is receiving increasing attention. The particulate matter is normally collected on a filter which is subsequently extracted with an organic solvent and then analyzed by various methods. The background levels (nanograms or lower) of PNA or other substances (i.e., phenols, nitrosamines, etc.) in the filters and solvents can be significant sources of error in analytical procedures.

In this paper we report the presence of these compounds in most of the readily available filter media as well as in analytical grade solvents used to extract the filters. The presence of these compounds becomes apparent only upon concentration to a few milliliters volume of about 150 milliliters of the solvent itself or after use of the solvent in extracting an unused filter. The analysis is by means of high performance liquid chromatography using an ultraviolet fluorescence or absorption detector. Filters used in collection or in extraction were made of teflon, glass fiber, callulose and organic polymers and solvents investigated were benzene, $CHCl_3$, CH_2Cl_2, hexane and cyclohexane. The effects of heat treatment on glass fiber filters is also noted. Finally a recommended procedure to purify and evaluate the solvent and to choose the filter media is offered.

INTRODUCTION

The polynuclear aromatic hydrocarbon (PNA) content of particulate matter emitted into the air from the combustion of fossil fuels or other processes is receiving increasing attention. The particulate matter, which absorbs these species, is normally collected on a filter which is subsequently extracted with an organic solvent and then analyzed by various methods. The presence in the filter or solvent of PNA or other substances (phenols, nitrosamines, etc.) even in the nanogram concentration range and lower can be a significant source of error in the analytical procedure.

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Filters used to collect the particulate matter may be made of teflon, glass fiber, cellulose or organic polymers. In addition, binders may be added. Solvents used in extraction procedures include benzene(1-2), methylene chloride(3-4), chloroform(5), hexane, and cyclohexane(6-8). After extraction, the solvent with the extracted material is usually reduced in volume by vacuum distillation or evaporation to make a more concentrated extract. In this way impurities originally present in the solvent or extracted from the filter material are also concentrated. The concentrated extract may be analyzed by high performance liquid chromatography (HPLC), gas chromatography, spectral methods (NMR, UV, IR) or wet chemical procedures used, for example, in the analysis of nitrosamines. In the nitrosamine procedure(9), diisopropylether is used and hence the presence of nitrosamines or other organic bound nitrogen in this solvent is of concern. In this paper, we discuss the presence of interfering substances in many of these filter materials and solvents which have been established by ultraviolet and fluorescence detection methods with the HPLC and by the nitrogen-phosphorous detector (rubidium bead) in the nitrosamine procedure. Recommendations for purification of solvents and choice of filters are given.

EXPERIMENTAL METHODS

Solvents

To evaluate solvents for possible interfering contaminants, a volume of 150 ml of the solvents benzene, n-hexane, cyclohexane, chloroform or methylene chloride (all Fisher reagent grade) is reduced to a volume of 2 to 3 ml by means of vacuum distillation. This procedure serves to concentrate the impurities with high boiling points and prevents decomposition of either the solvent or impurities. The concentrated solution of the possible contaminants is now analyzed using a Dupont Model 830 High Performance Liquid Chromatograph with a Dupont Model 835 Multiwavelength Photometer ultraviolet absorption and fluorescence detector. In our unit, the 254 nm wavelength was used. The column used was packed with octadecylsilane (ODS) at 50°C with 80:20 methanol-water as the mobile phase at 2000 psig. This procedure was used to detect polynuclear aromatic compounds. Known compounds containing 3, 4, 5, and 6 fused rings were analyzed to determine retention times and sensitivities on both detectors for purpose of identification and quantification. For those solvents containing impurities, redistillation in glass of a fresh batch was carried out followed by concentration and analysis of impurities as before. For nitrosamine analyses, diisopropylether is used to extract these substances and others from a phosphoric acid-water solution(5). Therefore, diisopropylether was analyzed using a Perkin-Elmer Model 3920B Gas Chromatograph equipped with a nitrogen-phosphorous detector. The column was 6' x 1/8" O.D. stainless steel packed with 10% KOH + 10% Carbowax 1540 on 60-80 mesh Gas Chrom Q maintained at 125°C for four minutes and then temperature programmed to 159° at 2°/minute.

Gelman Type GF/A glass filter, Gelman Type GF/E glass fiber, Whatman GB/B glass fiber, Millipore Standard (mixed esters of cellulose with a triton surfactant), Millipore Teflon with polyvinyl chloride or polypropylene backing and Millipore Mitex Teflon filters were studied. Cellulose thimbles for use in Soxhlet extraction were also evaluated. These filters or thimbles were extracted with 150 ml of contaminant free n-hexane in a Soxhlet extractor for 16 hours. The contaminant-free hexane was double distilled in glass. The extracting solvent was then reduced in volume to about 1.5 ml and analyzed in the same manner as in the study of the solvents.

In addition, the glass fiber filters were evaluated for the effect of heat to remove contaminants. The filters were placed in a muffle furnace for two hours at 500°C prior to extraction with n-hexane as before.

RESULTS

Table B-1 lists the retention times and sensitivities for known PNA compounds using the HPLC with the fluorescence and ultraviolet absorption detectors. Table B-2 gives the retention times and relative responses of contaminants found in the various solvents after concentration. In some cases, the specific peaks projected from a broad absorption band. Redistillation of some of the more promising solvents was carried out in glass and concentration/analysis was then repeated. These results are also in Table B-2 for n-hexane. Other solvents showed little improvement.

TABLE B-1. KNOWN COMPOUNDS - RETENTION TIME* AND SENSITIVITIES

Compound	Retention Time (Min./Sec.)	Response** (Peak Height, in.) U.V. Abs.	Fluorescence
Naphthalene	3:42	----	19.2
Anthracene	4:54	64.8	2611
Fluoranthene	5:12	182.4	41778
Pyrene	6:00	34.8	190
Chrysene	7:36	4.1	12.8
Bene (e) pyrene	10:48	47.2	256
Bene (a) pyrene	11:48	29.6	15974
Dibenzo (ah) anthracene	13:12	30	671
Benzo (ghi) perylene	17:22	256	10445

*HPLC, 25 cm X 2.3 mm I.D. stainless steel column, octadecylsilane (ODS) at 50°C, 80:20 methanol-water mobile phase, pressure 2000 psig.

**10 ul injection containing 10^{-6} grams of compound.

TABLE B-2. SOLVENT IMPURITIES

Solvent	Retention Time of Impurity (Min./Sec.)	Response* (Peak Height) In. U.V. Abs.	Response* (Peak Height) In. Fluorescence
$CHCl_3$, Reagent	1:15	4	9.6
	3:20	38	76.8
	6:30	Trace	16
CH_2CL_2, Reagent	2:40	20	64
	4:15	3.2	192
	6:15	Trace	16
	6:50	Trace	12.8
	8:30	Trace	11.5
	9:20	Trace	6.4
	10:00	Trace	12.8
	13:30	Trace	7.7
	14:40	Trace	6.4
Benzene, Reagent	3:20	34	960
	3:50	8	1741
	4:05	2	----
	5:15	6	25.6
	6:30	0.2	28.2
	7:10	0.24	----
	8:00	Trace	12.8
	8:30	Trace	----
	9:35	0.05	9.6
	11:00	0.05	3.2
	12:00	----	6.4
	12:30	----	6.4
	13:00	----	----
	13:30	----	4.8
	16:50	----	8
Cyclohexane, Reagent (large absorption band UV between 2-9 min., ave. 3")	3:00	0.5	----
	3:54	0.5	----
	5:30	4	19.2
	11:15	2.5	----
n-hexane, Reagent (large absorption band between 3-11 min. ave. 1.7" and 41" for UV and fluor.)	4:00	0.5	----
	4:15	0.5	----
	5:00	2.5	70.4
	5:20	2.5	----
	6:30	1.5	70.4
	7:30	0.7	73.6
	9:00	0.7	64.0
n-hexane, Redistilled (large absorption band between 5.5-9 min. in fluor. ave. 12.8")	5:20	----	6.4
	9:00	1.2	----

*HPLC, 10 ul injection of concentrated solvent. Same conditions as in Table B-1. Responses are peak heights above large bands, if any.

Baker reagent grade diisopropyl either was found to have a significant impurity which could be greatly reduced by twice redistilling the solvent in glass with elimination of the last 10% of the distillate. The impurity decreased by a factor of 20 to a level of 10 ug/ml. Table B-3 shows the retention and sensitivities for certain nitrosamines and the solvent impurity. The response of the nitrogen-phosphorus detector to the impurity is based on the assumption of a similar sensitivity to N, N-nitrosamines.

Table B-4 gives the retention times and relative responses of impurities found in the n-hexane extract of the various filters and thimble after concentration. In some cases, specific peaks projected from broad absorption bands. No measurable peaks were found in the concentrated extract from the heated Gelman GF/A Glass Fiber filter. This filter was chosen because it had the least contaminants as shown in Table B-4. Unfortunately, the filter became brittle in the heating process and not practical to use for our application. Specific identities of contaminants in the solvents and filters are not known. Many are likely to be PNA compounds based on their retention times. In any case they would interfere in analyses of PNA compounds.

CONCLUSIONS

1. Glass distilled n-hexane was found to be the best solvent for use in HPLC/fluorescence - UV detection work. Cyclohexane could be used, after purification. The chlorinated solvents and benzene were not satisfactory even on redistillation in glass.

2. Diisopropylether may be suitable for use in nitrosamine analysis(6) after redistillation.

3. Preheated Gelman GF/A glass fiber filters, and the Millipore Mitex Teflon 5 and 10 micron filters were found to be suitable for work as far as PNA contamination is concerned using the HPLC/Fluorescence - UV absorption detectors. The Teflon filter is favored because of the brittleness of the heat treated glass fiber filter.

4. It is recommended that filter media and solvents be evaluated by the procedures given to determine their usefulness for the specific analyses to be carried out.

TABLE B-3. RETENTION TIMES OF NITROSAMINES

Compound	Retention Time Sec.	Peak Are for 1^{ul} of 100 ppm Nitrosamine
Solvent impurity	211	949881
N, N - Diethylnitrosamine	400	399274
N, N - Diisopropylnitrosamine	662	283542
N, N - Dibutylnitrosamine	1106	207314

Instrument:	Perkin Elmer Model 3920B Gas Chromatograph with nitrogen-phosphorus detector
Column:	6' X 1/4" O.D. stainless steel packed with 10% Carbowax 1540 on Gas Chrom Q maintained @ $125^{o}C$ for 4 minutes and then programmed to $159^{o}C$ @ 2^{o}/min.
Flow:	Column - H_2 @ 5 psi and 2 ml/min; Air @ 44 psi and 100 ml/min; Carrier - He @ 15 ml/min.
Data Output:	Autolabs System IV Computing Integrator

TABLE B-4. FILTER IMPURITIES

Filter	Retention Time* of Impurity (min./sec.)	Response* (Peak Height) in. U.V. Abs.	Fluorescence
Gelman Type GF/A (Large band between 3-11 min. average 2.4" and 64" for UV and fluor.)	3:30	0.8	----
	4:15	0.4	----
	5:00	0.4	----
	6:45	----	9.6
	8:00	0.6	32
	9:00	0.8	Trace
	9:45	1.2	19.2
Gelman Type GF/E (Large band between 3-11 min. average 3" and 96" for UV and fluor.)	3:30	1.4	----
	4:15	1.9	----
	5:00	0.3	----
	6:45	2.3	22.4
	8:00	0.3	22.4
	9:00	0.2	----
	9:45	0.8	51.2

(Continued)

TABLE B-4 (Continued)

Filter	Retention Time* of Impurity (min./sec.)	Response* (Peak Height) in.	
		U.V. Abs.	Fluorescence
Millipore Teflon 3 (polypropylene) (Large band between 3-11 min. average 2.8" and 51.2 for UV and fluor.)	2:20	4.8	----
	2:35	4.8	64
	3:00	52	6.4
	3:15	----	6.4
	3:40	3.2	----
	4:15	2	44.8
	5:15	0.4	----
	5:50	2.4	----
	6:15	----	102.4
	7:45	----	6.4
	8:15	4.4	----
	8:30	4.4	12.8
	10:00	----	6.4
	10:30	1.2	----
	12:50	0.6	----
	15:15	0.8	----
Standard Millipore (Large band between 3-11 min. average 1.6" and 41.6" for UV and fluor.)	2:30	2.8	12.8
	3:15	----	12.8
	3:40	----	Trace
	3:48	----	102.4
	4:45	----	320
	5:30	0.8	166.4
	6:00	0.6	19.2
Millipore PVC	No peaks but PVC soluble in chlorinated solvents and limited to 100°C.		
Whatman GF/B (Large band between 3-11 min. average 8" and 352" for UV and fluor.)	1:12	2.4	----
	1:50	0.8	----
	2:24	0.4	----
	3:12	----	12.8
	3:50	1.2	192
	4:30	0.4	128
	5:05	----	32
	6:30	0.4	----
Millipore Mitex	None detected		
Cellulose Thimble (Large band between 3-11 min. average 2" and 104" for UV and fluor.)	0:42	0.9	----
	1:04	10.4	----
	1:50	0.5	4.8
	2:25	----	8
	2:40	----	4.8
	3:00	0.1	----
	3:24	0.3	----
	3:34	0.5	105.6

*HPLC, 10 ul injection of concentration n-hexane extract. Same condition as in Table B-1.

Responses are peak heights above large bands, if any.

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